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CXXIII. — CERTAIN DERIVATIVES OF METADIBROMDINITROBENZOL.[1]

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The dibromdinitrobenzol, melting at 117°.4, was made by Körner in his classical research on "Isomerism of the Aromatic Compounds with Six Atoms of Carbon,"[2] but its constitution has not been determined with certainty. Nietzki and Schedler,[3] in a recent paper, have proved that the dichlordinitrobenzol, melting at 103°, has the structure $Cl_2$1.3.$(NO_2)_2$4.6, and as this substance is made from the action of fuming nitric acid on metadichlorbenzol, just as the dibrom compound is made from metadibrombenzol, there is good reason to believe that they have the same constitution; but we thought it necessary to prove that this was the case before we studied this dibromdinitrobenzol further. For this purpose we heated the substance with aniline, and obtained the dianilidodinitrobenzol melting at 186°, which Nietzki and Schedler had ob-

[1] Presented to the American Academy of Arts and Sciences, December 13, 1899.
[2] Gazz. chim. ital., 1874, 305.
[3] Ber. d. chem. Ges., 30, 1666 (1897).

tained from their dichlordinitrobenzol; the dibrom substance therefore has the structure $Br_2$1.3.$(NO_2)_2$4.6. If aniline acted on the dibromdinitrobenzol in the cold, a bromanilidodinitrobenzol, $C_6H_2BrC_6H_3NH(NO_2)_2$, melting at 157°, was obtained, and this occurs in a yellow and in a red modification, which seem to differ in crystalline form as well as in color. This seems to be a case of dimorphism, as the two forms pass into each other with great ease. The yellow form is converted into the red by crystallization from benzol, the red into the yellow by heating to 135°. Similar phenomena have been observed in the cases of anilidotrinitrophenyltartronic ester[1] and trianilidodinitrobenzol.[2]

After the constitution of the 1.3.4.6 dibromdinitrobenzol had been determined, we studied the action of sodic ethylate upon it, in the hope of encountering the replacement of bromine by hydrogen under the action of this reagent, which has been studied for some years in this laboratory. But no such behavior was observed; the action ran in the normal way, resulting in the formation of dinitroresorcindiethyl ether melting at 133°, discovered by Warren and one of us,[3] and proved to have the symmetrical structure by Koch and one of us;[4] so that this observation confirms the determination of the constitution of this body by the action with aniline.

Sodic phenylate converted the dibromnitrobenzol into diphenoxydinitrobenzol, which melts at 129°. The action of sodic malonic ester was tried on this compound to determine whether the phenoxy groups could be replaced by the malonic ester radical $CH(COOC_2H_5)_2$; as it has been found[5] that the best way to make dichlordimalonicesterquinone,

$$C_6Cl_2[CH(COOC_2H_5)_2]_2O_2,$$

is by treating dichlordiphenoxyquinone with sodic malonic ester, and we wished to see whether the nitro groups would produce the same effect as the oxygen atoms of the quinone in promoting the replacement of the phenoxy groups by malonic

[1] Jackson and Bentley: This JOURNAL, **14**, 348.
[2] Jackson and Herman: *Ibid.*, **16**, 37.
[3] *Ibid.*, **13**, 170.
[4] *Ibid.*, **21**, 510.
[5] Jackson and Grindley: *Ibid.*, **17**, 597.

ester radicals. We found that phenol was eliminated when the diphenoxydinitrobenzol was treated with sodic malonic ester, and from the very unmanageable product a sodium salt was obtained which contained an amount of sodium corresponding to $C_6H_2OC_6H_3CNa(COOC_2H_5)_2(NO_2)_2$; so that we feel justified in assuming that the reaction has consisted in the replacement of the phenoxy by the malonic ester group.

The dibromdinitrobenzol, when reduced with zinc dust and acetic acid, gave a dibrommetaphenylenediamine, which was identical with that melting at 135° obtained by the action of bromine on metaphenylene diacetamide.[1] It follows from our preparation of this base that it has the constitution

$$Br_2.1.3.(NH_2)_2.4.6.$$

In all this work we have been careful not to approach too near to the field reserved by Nietzki and Schedler in their paper on dichlordinitrobenzol.

Preparation of Metadibromdinitrobenzol.

Monobromacetanilide was first made by passing a stream of air laden with the vapor of bromine through 5 liters of water in which 50 grams of acetanilide were suspended. The end of the reaction was determined by the appearance of a lasting yellow color in the liquid and a distinct change in the appearance of the solid. In all our attempts to convert this product into the dibromacetanilide by the action of liquid bromine on it when suspended in water, we observed the formation of a considerable amount of symmetrical tribromaniline,

$$(NH_2.1.Br_2.2.4.6.),$$

produced undoubtedly by the action of bromine on the free base proceeding from the saponification of some of the bromacetanilide by the hydrobromic acid formed in the reaction. The monobromacetanilide was accordingly filtered out, and, after being dried, suspended in glacial acetic acid or chloroform, to which a little more than the calculated amount of bromine was then added, drop by drop. This method gave an excellent yield of the dibromacetanilide with little trouble.

[1] Jackson and Calvert: This JOURNAL, 18, 482.

The dibromacetanilide was saponified by boiling it with sulphuric acid, of sp. gr. 1.44, in a flask with a return condenser, until the solution of the solid, which was usually accompanied by a darkening color, showed that the reaction was complete. The liquid was then allowed to cool, when most of the dibromaniline crystallized out, and what remained in solution was precipitated by the addition of a large quantity of water.

To remove the amido group, 100 grams of the dibromaniline were suspended in a mixture of 300 cc. of alcohol and 120 cc. of benzol, to which 20 cc. of sulphuric acid had been added; the mixture was heated in a flask on the steam-bath and 60 grams (a large excess) of solid sodic nitrite added as fast as the reaction would permit. The contents of the flask, which had taken on a reddish color, were boiled for an hour, and then allowed to stand over night, after which a large quantity of water was added, and the precipitated oily liquid distilled over with steam. A small amount of tribrombenzol is usually present, which appears as a solid in the condenser toward the end of the distillation with steam; it is well to stop the distillation as soon as this solid appears. The distillate with steam was dried with calcic chloride and distilled, and the fraction boiling from 210° to 225° collected for use. A small additional amount of dibrombenzol was obtained by extracting with ether the aqueous portion of the steam distillate, but the increase of the yield in this way was so small that this extraction was hardly worth while.

The dibrombenzol was converted into dinitrodibrombenzol by boiling it with fuming nitric acid, of sp. gr. 1.52, or better, a mixture of this acid and sulphuric acid. As soon as the oil had dissolved in the acid the reaction was complete; the boiling was stopped, and the product precipitated by pouring the acid liquid into a large quantity of cold water. The yellow crystals thus obtained were purified by crystallization from alcohol, until they showed the constant melting-point, 117°.

Determination of the Constitution of Metadibromdinitrobenzol by the Action of Aniline.

Two grams of the dibromdinitrobenzol, melting at 117°, were heated with an excess of aniline on the steam-bath for

half an hour. At the end of this time the excess of aniline was removed by treatment with dilute hydrochloric acid, and the yellow residue, after being washed thoroughly with water, was recrystallized from a mixture of alcohol and benzol until it showed the constant melting-point 185°, which is essentially identical with 186°, that of the dianilidodinitrobenzol prepared from dichlordinitrobenzol by Nietzki and Schedler.[1] As they established the constitution $(NHC_6H_5)_2 1.3.(NO_2)_2 4.6$ for this body, the dibromdinitrobenzol, melting at 117°, must have the corresponding structure, $Br_2 1.3.(NO_2)_2 4.6$.

Action of Aniline on Symmetrical Dibromdinitrobenzol in the Cold: Bromanilidodinitrobenzol.

Two grams of the dibromdinitrobenzol, cooled by a freezing-mixture, were moistened with aniline, and the mixture was allowed to stand packed in ice for twelve to eighteen hours. The excess of aniline was then removed by dilute hydrochloric acid, and the dense yellow residue, after thorough washing with water, was purified by crystallization from alcohol and benzol until it showed the constant melting-point of 157°, when it was dried at 100° and analyzed with the following result:

I. 0.0994 gram substance gave, by the method of Carius, 0.0558 gram AgBr.

II. 0.2138 gram substance gave 0.1229 gram AgBr.

	Calculated for $C_6H_3BrC_6H_3NH(NO_2)_2$.	Found. I.	II.
Br	23.67	23.89	24.46

Properties of Bromanilidodinitrobenzol,
$C_6H_3BrC_6H_3NH(NO_2)_2$ $(Br1.C_6H_3NH3.(NO_2)_2 4.6.)$.

This substance crystallizes from a mixture of benzol and alcohol, sometimes in much modified short and thick flat prisms, apparently of the monoclinic system, resembling certain crystals of feldspar; at other times in rhombic plates, occasionally with some of the angles slightly beveled, which pass into forms like rhombohedra; all of these crystals have a full golden-yellow color. Other crystals were distinguished from these by their brilliant red color and by appearing in

[1] Ber. d. chem. Ges., 30, 1668 (1897).

square prisms, modified on one of their angles or on two opposite angles. From these two colors, red and yellow, and the difference at least in crystalline habit, if not really in crystalline form, we infer that the substance appears in two closely related modifications. The yellow form, in which the substance is obtained from its preparation, becomes gradually converted into the red by crystallization from a mixture of alcohol and benzol, but several crystallizations are necessary to make this conversion complete. If, however, the yellow form is dissolved in benzol alone, the solution deposits, as it evaporates, a red oil, which, on stirring, solidifies to the red crystals. All the other common organic solvents, except the alcohols, also convert the yellow into the red form by a single crystallization. On the other hand, if the red crystals are heated in an air-bath, they begin to assume a yellow color at 110°, and are completely converted into the yellow form at 135°; this conversion is attended with no change in weight. The substance melts at 157°, forming a red liquid, which, when cooled and stirred, solidifies to the yellow modification. It is obvious that the melting-point given above is that of the yellow form, since the red is converted into the yellow at 135°. The bromanilidodinitrobenzol is freely soluble in benzol, soluble in toluol or chloroform, slightly soluble in ether, acetone, amyl alcohol, or hot ethyl alcohol. The best solvent for it is a mixture of benzol and alcohol.

Determination of the Constitution of Metadibromdinitrobenzol by Treatment with Sodic Ethylate.

One gram of the dibromdinitrobenzol, melting at 117°, was mixed with an excess of sodic ethylate, prepared by the action of sodium on a considerable excess of absolute alcohol, and after the mixture had stood for some time at ordinary temperatures the excess of alcohol was allowed to evaporate spontaneously. The residue, after repeated washings with hot water, was purified by crystallization from a mixture of ligroin and benzol, when it was found to melt at 133°, the melting-point of the dinitroresorcinediethyl ether, discovered by Warren and one of us,[1] which it also resembled in crystalline

[1] This JOURNAL, 13, 170.

form. As Koch and one of us[1] have proved that this dinitroresorcinediethyl ether has the constitution

$$(OC_2H_5)_2 1.3.(NO_2)_2 4.6,$$

it follows that the dibromdinitrobenzol, melting at 117°, has the constitution $Br_2 1.3.(NO_2)_2 4.6$, a result which confirms that already obtained from the action of aniline.

Action of Sodic Phenylate with Symmetrical Dibromdinitrobenzol.

The sodic phenylate for this experiment was prepared by adding 5 grams of powdered sodic hydrate to enough melted phenol to make a pasty mass. While this was still in the viscous state, 5 grams of the dibromdinitrobenzol were added little by little with constant stirring, the beaker containing the mixture being kept cool with ice-water. The product, a dark-brown, solid mass, was treated with water, filtered, and the insoluble portion recrystallized either from slightly dilute alcohol or from a mixture of benzol with a large excess of ligroin, until it showed the constant melting-point 129°, when it was dried *in vacuo*, and analyzed with the following results:

I. 0.2494 gram substance gave, on combustion, 0.5563 gram CO_2 and 0.0903 gram H_2O.

II. 0.3746 gram substance gave, on combustion, 0.8457 gram CO_2. The water was unfortunately lost.

	Calculated for $C_6H_2(OC_6H_5)_2(NO_2)_2$.	Found. I.	II.
C	61.38	60.82	61.59
H	3.41	4.02	....

The method of making sodic phenylate given above was adopted because in alcoholic solution the sodic phenylate gave principally the dinitroresorcindiethyl ether, and in aqueous solution there was no action until high temperatures were reached, and then the yield was unsatisfactory.

Properties of the Dinitroresorcindiphenyl Ether,
$C_6H_2(OC_6H_5)_2(NO_2)_2$. $((OC_6H_5)_2 1.3.(NO_2)_2 4.6.)$.

This substance, when crystallized from a mixture of benzol and alcohol, forms slender white prisms terminated by one

[1] *Ibid.*, **21**, 510.

slanting plane, or, when better developed, by two planes meeting at a very obtuse angle and modified by several smaller ones, so that a blunt end is formed. It melts at 129°. It is freely soluble in benzol; soluble in cold toluol or chloroform, or in alcohol, ligroin, or acetone when these solvents are hot; slightly soluble in ether or amyl alcohol. The best solvent for it was either dilute alcohol or ligroin containing a little benzol.

Some experiments were tried to determine whether the phenoxy groups in the diphenoxydinitrobenzol could be replaced by malonic ester radicals ($CH(COOC_2H_5)_2$), as a replacement of this sort had been observed in the case of dichlordiphenoxyquinone.[1] The solid diphenoxydinitrobenzol was dissolved in an alcoholic solution of sodic malonic ester, and the mixture allowed to stand at ordinary temperatures over night; afterward it was treated with dilute sulphuric acid, which precipitated an oil, and showed that phenol had been set free by the strong smell of this substance. The oily precipitate, after washing with water, was extracted with ether, which removed from it a pale-yellow oily substance; but as this did not solidify, even after standing for several months, we tried to determine its nature by the analysis of a salt. A specimen of the oil was dissolved in alcohol and treated with an aqueous solution of sodic hydrate, which threw down a bright-red precipitate; this was washed with benzol, dried *in vacuo*, and analyzed with the following results:

I. 0.1383 gram substance gave 0.0191 gram Na_2SO_4.
II. 0.1476 gram substance gave 0.0228 gram Na_2SO_4.

	Calculated for $C_6H_2(NO_2)_2OC_6H_5CNa(COOC_2H_5)_2$.	Found. I.	II.
Na	5.23	4.47	5.01

The results of these analyses, in connection with the elimination of phenol, prove that the reaction has run as was expected. The phenoxydinitrophenylmalonic ester separated from the salt as an oil, and therefore we did not think it worth while to attempt a more careful study of it.

[1] Jackson and Grindley: This JOURNAL, 17, 597.

Reduction of Symmetrical Dibromdinitrobenzol with Zinc Dust and Acetic Acid.

Twenty grams of zinc dust were placed in a flask fitted with a Bunsen valve and connected with a carbonic dioxide generator, acetic acid of 85 per cent was added, and then 5 grams of the dibromdinitrobenzol in small portions at a time, as under these conditions the reaction ran quietly and smoothly, although accompanied by blackening in every case. The reduction was carried on at first in the cold, but toward the end of the operation the mixture was heated gently on the steam-bath. After two hours the reaction was complete, when the insoluble portion was filtered out and extracted with dilute alcohol, which, upon cooling, deposited crystals melting even in the crude state at 131°. The filtrate from the insoluble reduction-products was treated with an excess of sodic hydrate sufficient to dissolve the zinc salts, the precipitate formed in this way filtered out and extracted with hot dilute alcohol, which gave another portion of the crude product melting at 131°. After purification, by crystallization from alcohol, the melting-point became constant at 134°; it was dried *in vacuo*, and analyzed with the following result:

0.1407 gram substance gave, by the method of Carius, 0.1976 gram of AgBr.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Br	60.15	59.78

This dibromphenylenediamine melts practically at the same point (135°) as that prepared by S. Calvert and one of us[1] from metaphenylenediacetamide and bromine. It also crystallizes like this in white needles, which turn brown on exposure to the air. As the constitution of our dibromdinitrobenzol is $Br_2$1.3.$(NO_2)_2$4.6, it follows that this dibrommetaphenylenediamine must have the corresponding constitution,

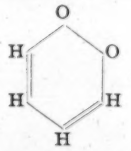
$$Br_2\text{1.3.}(NH_2)_2\text{4.6.}$$

[1] This JOURNAL, 18, 482.

CXXIV.—ON CERTAIN DERIVATIVES OF ORTHOBENZOQUINONE.[1]

By C. Loring Jackson and Waldemar Koch.

Attempts to prepare the orthobenzoquinone,



have been mentioned, so far as we can find, in only two papers. The first is that by Zincke,[2] in which he describes tetrabromorthoquinone and tetrachlororthoquinone, but says that a number of attempts to make the unsubstituted orthoquinone have failed to produce the desired result. The second is by Hinsberg and Himmelschein,[3] who obtained orthodioxydiphenylsulphone by the action of potassic dichromate on a mixture of pyrocatechin and benzolsulphinic acid, and draw the inference that the formation of this substance probably was preceded by the formation of orthoquinone. They add that all their experiments to isolate orthoquinone have failed because of its strong tendency to condensation and polymerization.

It seemed to us that one probable cause of the ill success of these experiments was the sensitiveness of the orthoquinone to oxidizing agents; this view was confirmed by the observations of Cousin,[4] that trichlorpyrocatechin and dibrompyrocatechin give only red resinous products with nitric acid, whereas the trichlor- or tribromhomopyrocatechin gives under the same conditions an orthoquinone; and also by some experiments undertaken by H. A. Torrey and one of us on the action of hydric dioxide or electrolytic oxygen on pyrocate-

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Waldemar Koch. It was presented to the American Academy of Arts and Sciences May 9, 1900.

[2] Ber. d. chem. Ges., **20**, 1776 (1887).

[3] *Ibid.*, **29**, 2025 (1896).

[4] Ann. chim. phys., (7), **13**, 485.

chin, which led to unpromising black products. Accordingly, we searched for a method which would produce a quinone without the use of an oxidizing agent, and found one in the action of iodine on the lead salt of the dioxybenzol. After having shown that the method converted hydroquinone into quinone, we applied it to pyrocatechin ; but our first experiments led to no results, because we used alcohol as our solvent, which attacks the orthoquinone as soon as it is formed. Upon replacing the alcohol by chloroform we succeeded in obtaining a dark garnet-red solution, in which the presence of orthobenzoquinone was established by a number of tests given later in this paper.

From this solution we next tried to isolate the solid orthoquinone but, after trying every method we could devise, which gave even a remote promise of success, we have failed to obtain a trace of solid orthoquinone, and are forced to the opinion that it cannot exist in the solid state, or even for any length of time in solution. The products obtained in place of the orthoquinone in every case were a black substance insoluble in chloroform, and a brown substance, or mixture of substances, which dissolved in chloroform ; this brown product we have not attempted to investigate, but we have studied the black insoluble product and can give a fairly complete account of its nature in spite of its unsatisfactory properties. It begins to form in the chloroform solution of the orthoquinone in less than an hour, and is best obtained by allowing the solution to stand in a corked flask for not more than thirty hours. A combustion of the substance gave results corresponding to the formula $C_{12}H_8O_5$; the analysis of a lead salt prepared in a somewhat different way indicated the same formula, and this was confirmed by two analyses made by H. A. Torrey of his product from the electrolytic oxidation of pyrocatechin, which seemed to be identical with ours, and by an analysis of the benzoyl derivative of our black substance ; we have, therefore, five analyses of four different samples, all of which agree with each other, and leave no doubt that the substance is a definite compound and has the formula $C_{12}H_8O_5$. This formula indicates that the compound was formed by the union of 2 molecules of orthoquinone with the introduction of an ad-

ditional hydroxyl group, a view which is confirmed by the analysis of the lead salt, $C_{13}H_8O_4Pb$, in which there are evidently two benzol rings to each atom of lead. When we consider the manner in which these two benzol rings are united, two theories seem especially worthy of attention; first, the two rings may be joined directly, so that the compound is a substituted diphenyl:

$$(I)\quad O_2(HO)H_2C_6—C_6H_3(OH)_2;$$

or second, they may be united by 2 atoms of oxygen forming a substituted pyrocatechine ether according to this formula:

$$(II)\quad (HO)H_2C_6=O_2=C_6H_2(OH)_2.^{1}$$

The first (diphenyl) formula is rendered much more probable than the second by the analogy between our orthoquinone and the orthonaphthoquinone, which is converted by dilute sulphuric acid into dinaphthyldiquinhydrone,[2]

$$O_2H_6C_{10}—C_{10}H_3(OH)_2,$$

a black powder like our alteration-product; this has been proved by Korn[3] to be a dinaphthyl body by conversion into α-α-dinaphthyl and diphthalylic acid,

$$(COCO)(C_6H_4COOH)_2.$$

The support of the diphenyl formula by this analogy is so strong that we should feel it was hardly worth while to consider the second (ether) formula, if it were not for the fact that we have observed an oxygen attachment similar to that in Formula II in a derivative of tetrabromorthoquinone, described later in this paper. To decide between Formula I and Formula II we studied the action of reducing agents on the black substance, as, if it were an ether (Formula II), it should be reduced to a mixture of pyrocatechin and a trioxybenzol, whereas a diphenyl compound (Formula I) would only take up 2 atoms of hydrogen without decomposition.[4] We selected as the reducing agent sodium amalgam and

[1] In both these formulas the third hydroxyl group may be attached to the other benzol ring.

[2] Stenhouse and Groves: Ann. Chem. (Liebig), 194, 205.

[3] Ber. d. chem. Ges., 17, 3020.

[4] Korn did not succeed in splitting dinaphthyldiquinhydrone into simpler bodies by reduction. Ber. d. chem. Ges., 17, 3024.

water, because this had proved effective in breaking up the pyrocatechin ether containing bromine already alluded to; but, even after long-continued action on our black alteration-product, not a trace of pyrocatechin could be detected; the only reduction-product was a black substance evidently as complex as the original body. This result, therefore, declares decisively in favor of the diphenyl structure (Formula I).

The action of benzoyl chloride on the black substance in presence of sodic hydrate converted it into a tribenzoyl derivative, $C_{12}H_5O_3O_3(COC_6H_5)_3$, thus proving the existence of three hydroxyl groups in the substance; and this benzoyl derivative, and also the original black compound, gave new substances with phenylhydrazine, which contained nitrogen, as was shown by the analyses. Unfortunately, the percentage of nitrogen found in both cases was far below that required by the probable formulas, which is undoubtedly accounted for by the difficulty in purifying these amorphous and infusible substances; our analyses, therefore, amount only to qualitative proofs of the presence of nitrogen. The introduction of the nitrogen, however, makes it highly probable that both the original substance and its tribenzoyl derivative contain oxygen atoms in the quinone position. We feel justified from the results of the foregoing experiments in assigning to the black alteration-product the formula

$$O_2(HO)H_2C_6—C_6H_3(OH)_2,$$

in which two of the hydroxyl groups are probably in the ortho position to each other, since the substance forms a stable lead salt when treated with plumbic acetate.

We have made no progress toward determining the position of the third hydroxyl group, which may even be attached to the other benzol ring. The introduction of this third hydroxyl group is not without analogy, since the dinaphthylorthoquinone, $C_{10}H_5O_2—C_{10}H_5O_2$, is converted by the action of the air on its solution in weak alkali into the dioxy compound, $C_{10}H_4OHO_2—C_{10}H_4OHO_2$.[1] In our case, however, the oxygen of the air took no essential part in the reaction, as the same alteration-product was formed in an atmosphere of carbonic

[1] Korn: Ber. d. chem. Ges., 17, 3021.

dioxide; and this is not surprising, as we have had frequent occasion to observe that the orthobenzoquinone is a much stronger oxidizing agent than the orthonaphthoquinone, so that one portion of it might easily oxidize the other during the polymerization. The portions of the orthoquinone which gave up oxygen during the formation of the black body were undoubtedly converted into the brown substances soluble in chloroform, which made up about half of the total product.

Although, as has been already stated, we could not obtain the orthoquinone in the solid state, many of its properties can be determined from the study of its solution in chloroform; thus, there can be little doubt that it has an intense red color and little, if any, odor, as the solution smelt of nothing but chloroform, whereas a smell as strong as that of paraquinone could have been detected even in presence of the amount of chloroform used. Its very slight stability has been dwelt on at sufficient length already, but we should add that it seems to be decomposed at once by even small quantities of water or alcohol.

We turn next to the reactions of the solution on which is based our inference that it contained orthoquinone. Hydrochloric acid converted it into monochlorpyrocatechin, which, however, was mixed with a little pyrocatechin, as would be expected, since Wichelhaus[1] has shown that the action of hydrochloric acid on parabenzoquinone consists in the formation of hydroquinone and chlorine, which subsequently react together, and in this corresponding case part of the pyrocatechin formed could well have escaped the substituting action of the chlorine. Reducing agents like ammonic sulphide or sulphurous dioxide produced pyrocatechin from this chloroform solution. Bromine formed with it tetrabrompyrocatechin, the reduction of the orthoquinone being achieved in this case by the hydrobromic acid formed in making the substituted quinone.

When the chloroform solution was added, drop by drop, to a solution of benzolsulphinic acid, also in chloroform, an orthodioxydiphenylsulphone, $C_6H_5SO_2C_6H_3(OH)_2$, melting at 153°, was formed, which should be identical with that obtained by

[1] Ber. d. chem. Ges., 12, 1504.

Hinsberg and Himmelschein[1] by oxidizing pyrocatechin in presence of benzolsulphinic acid, but the properties of the two substances show they are different. Hinsberg and Himmelschein's substance contained water of crystallization, and melted at 117°, if this were not driven off; at 143° to 145° after heating in the steam-bath; and at 164°, if completely dried by previous fusion; our compound contained no water, and melted at 153°, whether dried at ordinary temperatures or by previous melting. We have not succeeded in finding the conditions under which Hinsberg and Himmelschein's compound is formed, so that we were unable to compare the two substances, and must consider with our present knowledge that they are isomeric.

With aniline the chloroform solution gave a dianilidoquinoneanil, $C_6H_3(C_6H_5NH)_2O(C_6H_5N)$, which melted at 203°, and by this and a careful comparison of its other physical properties was proved to be identical with the body prepared by Zincke and von Hagen[2] from paraquinone by the action of aniline and acetic acid. As this substance has previously been made only from paraquinone, it has always been supposed that it contains the oxygen and anil group in the para position to each other, but after our preparation of it from orthoquinone it is also possible that it is a derivative of orthoquinone; and some weight is given to this view by the fact that it is formed easily from the orthoquinone by aniline alone, whereas it can be prepared from the paraquinone only with difficulty, and by the combined action of aniline and acetic acid. On the other hand, it seems hardly probable that a derivative of orthoquinone would be so stable as this; and the β-naphthoquinone forms with aniline and alcohol a corresponding anilidonaphthoquinoneanil,

$$C_{10}H_5O(C_6H_5NH)(C_6H_5N),$$

which is undoubtedly a derivative of α-naphthoquinone. Zincke[3] also has obtained recently from the azimidodichlororthoquinone by warming it with aniline an azimidoanilidomonochloroxyparaquinone, and similar cases of conversion of

[1] Ber. d. chem. Ges., **29**, 2025.
[2] *Ibid.*, **18**, 785.
[3] Ann. Chem. (Liebig), **311**, 276.

orthoquinones into derivatives of paraquinones are not rare. We are so strongly of the opinion, therefore, that our dianilidoquinoneanil is a para body with the constitution

$$O,1.C_6H_5N,4.(C_6H_5NH)_2,2.5,$$

that we have not thought it worth while to submit the question to an experimental investigation, which would, of necessity, require much time. Assuming that the constitution given above is correct, the body would be formed from the orthoquinone by the following series of transformations, which are modeled after those worked out by C. Liebermann[1] for the corresponding case of β-naphthoquinone:

The replacement of the two hydrogen atoms of the orthoquinone by the anilido groups to form II. takes place under the oxidizing influence of another portion of the orthoquinone, which takes up hydrogen to form pyrocatechin (always formed in our process); II. then passes by isomerization into III., which is converted into IV. by the further action of aniline.

Upon treating the solution of orthoquinone with orthophenylenediamine no phenazine was formed, but the reaction seemed to consist only in the oxidation of the diamine.

[1] Ber. d. chem. Ges., 14, 1664.

We have also devoted some attention to the study of the tetrabromorthoquinone, and have obtained from it two derivatives. The first of these was prepared by treating tetrabromorthoquinone with tetrabrompyrocatechin dissolved in acetic acid and water; it was a beautiful red body, which was soluble only in warm nitrobenzol. Its ormula was $C_{12}Br_6O_4$, and it was formed by the following reaction,

$$C_6Br_4(OH)_2 + C_6Br_4O_2 = C_{12}Br_6O_4 + 2HBr,$$

as was shown by the detection of hydrobromic acid as one of the products of the reaction, and the fact that a good yield was obtained only when the two reagents were used in equal amounts. This formation of the substance is most naturally explained by supposing that the two benzol rings are united by two of the atoms of oxygen, forming a substituted pyrocatechin ether, $C_6Br_4{=}O_2{=}C_6Br_2O_2$, but it is also possible that the union took place directly between the two benzol rings forming a diphenyl compound with this formula, $O_2Br_2C_6{-}C_6Br_2O_2$, the 2 atoms of bromine removed in this reaction combining with the atoms of hydrogen of the pyrocatechin, and thus oxidizing it so that the body contains two orthoquinone groups. To decide between these two formulas the substance was submitted to reduction with sodium amalgam, as under these circumstances the pyrocatechin ether should be split into 2 molecules of pyrocatechin, while the diphenyl compound should be reduced without splitting the molecule. The principal product of this reduction was a chocolate-brown substance, which contained an amount of bromine nearly identical with that of the original body, and was converted into it again by nitric acid. With it there was always formed a certain amount of pyrocatechin, and this seemed to us strongly in favor of the ether formula, but it could not be considered conclusive, as the amount of pyrocatechin was much less than that of the brown product. In the hope of increasing the yield of pyrocatechin we submitted the brown product again to the action of sodium amalgam, but found it was entirely unaffected; we accordingly oxidized it to the original red body—a reaction which takes place quantitatively—reduced this again by sodium amalgam,

obtaining fresh quantities of pyrocatechin and the brown body, and continued these alternate reductions and oxidations until the original specimen of the red body had been completely converted into pyrocatechin. Although we could wish that this conversion had taken place by reduction alone, the use of the oxidations cannot be held to vitiate the argument, as they gave a quantitative yield of the original substance, and we feel justified, therefore, in inferring that the two benzol rings are united by two atoms of oxygen, and that the substance is a pyrocatechin ether.

The brown product formed by the action of sodium amalgam was also obtained by the action of tribrompyrogallol on the tetrabromorthoquinone, and of hydrochloric acid at 160° to 175° on the red pyrocatechin ether. There seems no doubt, therefore, that it is formed from the red body by the conversion of two orthoquinone oxygen atoms into hydroxyl groups; in other words, that it is the pyrocatechin corresponding to the red orthoquinone; and this view is confirmed by the oxidation of the brown substance to the red by nitric acid. The reaction of the hydrochloric acid is especially instructive in regard to the constitution of these two bodies, as it is the familiar conversion of a quinone to a hydroquinone by this reagent. The red color of the original substance also points to the presence of orthoquinone oxygen in it, whereas the lighter color of the reduction-product (brown when crystallized, but purplish-white when amorphous) confirms the view that it is the hydroxy compound. We therefore assign the following formulas and names to these substances: red compound, $Br_4C_6{=}O_2{=}C_6Br_2O_2$, hexabromorthoquinopyrocatechin ether; the brown reduction-product, $Br_4C_6{=}O_2 = C_6Br_2(OH)_2$, hexabromdiorthoxypyrocatechin ether. The only observed fact not in accordance with this last formula is that the substance does not dissolve in a solution of sodic hydrate, as we should expect it to do considering that it contains two phenol hydroxyls; this may, however, be explained by the very slight solubility of the substance (soluble only in warm nitrobenzol), which might prevent the solution of sodic hydrate from coming into sufficiently close contact with it to react.

The hexabromorthoquinopyrocatechin ether was formed when acetic acid or alcohol was used as the solvent, but none of it was obtained when the tetrabromorthoquinone and tetrabrompyrocatechin were mixed in solution in chloroform or ether. In this latter case the residue left after the evaporation of the solvent was a reddish white mass, apparently a mixture of the unaltered reagents, which contained none of the hexabromorthoquinopyrocatechin ether. This is strange, as Zincke, by mixing the two substances in ethereal solution, obtained a black crystalline substance. An attempt will be made in this laboratory next year to find the conditions under which this black compound is formed.

We have succeeded also in obtaining a reaction similar to that just described from tribromresorcin and tetrabromorthoquinone. The other phenols tried acted simply as reducing agents. The product proved to be a ditribrommetoxyphenyldibromorthoquinophenylene ether,

$$(C_6HBr_3OHO)_2C_6Br_2O_2.$$

This substance melts at 217°, and like the reduction-product just described, does not dissolve in a solution of sodic hydrate, in spite of the two phenol hydroxyl groups it contains, according to its most probable formula. We should explain this anomaly in the same way as before, although this substance is much more soluble than the reduction compound.

With glacial acetic acid the tetrabromorthoquinone, $C_6Br_4O_2$, formed a white compound, to which we have given much attention, but of which we can only give a very imperfect account. Zincke,[1] in his paper on tetrabromorthoquinone, noticed that it was attacked by glacial acetic acid, but did not isolate the product; on the other hand he obtained a white body by crystallizing tetrabromorthoquinone from ether and ligroin, which we have not succeeded in preparing. When tetrabromorthoquinone is evaporated to dryness with glacial acetic acid, a small amount of the red hexabromorthoquinopyrocatechin ether is formed, but the greater part of the quinone is converted into a white crystalline body melting at 230°, the analysis of which led to one of the two following for-

[1] Ber. d. chem. Ges., **20**, 1777.

mulas, $C_{14}H_2Br_8O_5$ or $C_{14}Br_8O_6$. The first would be formed by the union of 2 molecules of the tetrabromorthoquinone with 1 of acetic acid, 1 molecule of water being eliminated, thus:

$$2C_6Br_4O_2 + C_2H_4O_2 = C_{14}H_2Br_8O_6 + H_2O.$$

The second would be formed from the first by removing 2 atoms of hydrogen, which could be done by the oxidizing action of another portion of the tetrabromorthoquinone, and the tetrabrompyrocatechin thus formed would then give rise to the red body, which always accompanied the white product; but the amount of this red compound always fell far below that which should be formed, if it had taken such an important part in the reaction (10 grams of tetrabromorthoquinone should give 5 grams of the red product, whereas the usual yield was only 0.8 gram), and, as the amount of hydrogen found in the white compound was distinctly larger than should have been given by a body free from that element, we have decided to adopt provisionally the formula $C_{14}H_2Br_8O_5$. We had hoped to settle this question by studying the decomposition-products of this substance, but so far it has either been unaffected or completely decomposed by all the reagents we have tried. We hope that in the coming year the study of this body will be completed and the work carried on in various other directions in this laboratory.

EXPERIMENTAL PART.

Action of Iodine on the Lead Salt of Hydroquinone.

These experiments were tried to test the efficacy of this method of making quinones. An aqueous solution of 10 grams of hydroquinone was treated with the calculated amount of sodic hydrate in a flask, to which the air had access only through a tube containing an alkaline solution of pyrogallol; to the sodium salt thus formed an aqueous solution of plumbic acetate was added, which gave a white precipitate of the lead salt. As this blackened rapidly on exposure to the air, no attempt was made to filter it, but an alcoholic solution of 5 grams of iodine was added directly to the precipitate suspended in the liquid, when plumbic iodide was formed, as shown by the appearance of a yellow color. After the reac-

tion seemed to have come to an end, the insoluble substances were filtered out, and the filtrate, which had a strong odor of quinone, extracted with ether. This ether extract left, on evaporation, yellow crystals with a strong odor of quinone, which under the microscope showed the characteristic form of this substance, and after purification by sublimation melted at 112°–113°, which, although distinctly below the melting-point of quinone, 115°.7, is near enough to it to prove, in conjunction with the other properties, that quinone was formed.

To prove that this quinone was formed by the action of the iodine on the lead salt and not by the oxidizing effect of the air, a specimen of the salt mixed with water was exposed to the air for several hours, until it was thoroughly blackened; upon filtration a red solution was obtained which had no odor of quinone. Extraction with ether did not remove the red color, and on the evaporation of the ether, crystals of hydroquinone were obtained, recognized by the melting-point, but no quinone. Upon adding an alcoholic solution of iodine to a similar specimen of the lead salt blackened by exposure to the air, the sharp odor of quinone was observed at once, and a considerable amount of this body was obtained from the filtrate. The method, therefore, is applicable to the production of quinones, but naturally would be used only in cases where oxidation is inadmissible.

We also tried some experiments with iodine and the lead salt of resorcin, but as it was evident that the purification of the product would be a matter of great difficulty, we have postponed the continuation of this work until we have finished the study of pyrocatechin.

ORTHOQUINONE.

Action of Iodine on the Lead Salt of Pyrocatechin, Preparation of a Solution of Orthoquinone.

To prepare the lead salt of pyrocatechin 2 grams of pyrocatechin dissolved in 150 cc. of water were added gradually, with constant stirring, to a boiling solution of 7.5 grams of plumbic acetate in 250 cc. of water. The precipitated lead salt was allowed to settle, filtered out, and washed five times with hot water. It was then dried at 100° and finely pul-

verized. It is not advisable to use more than 2 grams of pyrocatechin at a time in making the lead salt, as with larger amounts it was found to be hard to wash out all the impurities.

Ten grams of this lead salt were thoroughly moistened with chloroform in a 500 cc. glass-stoppered flask. The salt must be absolutely dry, and the chloroform free from water and alcohol, as these substances decompose orthoquinone. A boiling solution of five grams of iodine in 200 cc. of chloroform was then added to the lead salt and the whole shaken well for five to ten minutes, after which, upon filtering through a dry Gooch crucible, a garnet-red solution of orthoquinone was obtained. The amount of iodine used in this experiment is a little more than half that required by the theory (1 molecule to each molecule of the lead salt). This large excess of the lead salt was used to avoid as far as possible the presence of iodine in the chloroform solution, and in this we were fairly successful, as a sample of it, when tested with a fresh specimen of the lead salt of pyrocatechin, showed only a trace of plumbic iodide.

This chloroform solution contained orthobenzoquinone, $C_6H_4O_2$1.2, as is proved by the experiments described later in this paper, and it must have been a nearly pure solution of this body, since the only other substance which could have been present was iodine, and the amount of this was very small, as shown in the preceding paragraph. It had a dark garnet-red color, and no odor could be perceived except that of the chloroform. Within an hour from the time of its preparation it began to show signs of alteration by depositing a black precipitate, and after twenty-four to thirty hours all the orthoquinone had disappeared from the solution. We have made numerous attempts to isolate the solid quinone from its solution in chloroform, of which the following is a brief summary: Evaporation spontaneously at ordinary temperatures; evaporation at $-12°$; evaporation *in vacuo* of a solution in pure chloroform made from chloral, so as to avoid all traces of alcohol which decomposes the orthoquinone; evaporation by a stream of dry air or dry carbonic dioxide passed through the

solution cooled by a freezing-mixture; precipitation with ligroin at —5°; precipitation with tetrachloride of carbon at —20°; we had great hopes of this last attempt, as we had not succeeded in making any of the orthoquinone, when tetrachloride of carbon was substituted for chloroform in the preparation, and we inferred from this that the quinone probably was insoluble in this substance; but this, as well as all the other experiments mentioned above, did not lead to the desired result. The product in every case was the black alteration-product already mentioned, the nature of which will be discussed presently, so that we are forced to the conclusion that the orthobenzoquinone cannot exist for any length of time, if at all, in the solid state.

STUDY OF THE ALTERATION-PRODUCT OF ORTHOBENZOQUINONE.

This substance was most conveniently obtained by allowing the chloroform solution of orthobenzoquinone, prepared as already described, to stand at ordinary temperatures in a corked flask from twenty-four to thirty hours.[1] The black precipitate thus formed was not easy to purify, for although it was soluble in alcohol and some other solvents, all our attempts to crystallize it have failed; we finally decided to depend for its purification on its insolubility in chloroform and benzol. Accordingly, after filtering it out from the chloroform in which it was formed, we washed it thoroughly with chloroform and afterward extracted it three times with hot benzol. About 40 per cent of the orthoquinone used was converted into this black product. In calculating this yield we assumed that the amount of orthoquinone in the chloroform solution corresponded to the amount of iodine used in making it. The black substance, after it had been purified by extraction with benzol, was dried *in vacuo* and analyzed with the following results:

0.2041 gram substance gave, on combustion, 0.4684 gram CO_2 and 0.0696 gram H_2O.

[1] The solution should not be allowed to stand more than thirty hours, as in that case the product is contaminated with a brown impurity.

	Calculated for $C_{12}H_6O_2(OH)_2$.	Calculated for $C_{12}H_6O_3(OH)_2$.	Found.
C	66.67	62.07	62.59
H	3.70	3.45	3.79

These numbers would indicate that the substance has been formed by the union of 2 molecules of orthoquinone with the introduction of a hydroxyl group, but it is obvious that the composition of a body like this, which is amorphous and has no definite melting-point, can be determined only by the analysis of several samples prepared by different methods. Accordingly, we undertook the preparation and analysis of the lead salt, which should be insoluble and stable, if the substance contains two hydroxyls in the ortho position to each other, as would be the case if it is formed from 2 molecules of orthoquinone. Further, as we thought that the additional hydroxyl indicated by the analysis might have been introduced by the action of the oxygen of the air, we repeated the preparation in an atmosphere of carbonic dioxide. The solution of orthoquinone was made from the lead salt of pyrocatechin and iodine in a flask filled with this gas, and was separated from the plumbic iodide by means of a rose filter with an asbestos film without exposing it to the air. Upon standing over night, still in an atmosphere of carbonic dioxide, a black precipitate was formed, identical in appearance with that obtained by the ordinary process. This was purified in the way already described, and then converted into its lead salt as follows: 0.3 gram of this black body dissolved in 40 cc. of alcohol was added to a boiling solution of 1 gram of plumbic acetate in 400 cc. of water; this large amount of water is necessary to prevent the alcohol from precipitating plumbic acetate, which, becoming imprisoned in the lead salt, could hardly be removed by washing. The jet-black lead salt thus obtained was washed five times with hot water, dried at 100°, and analyzed with the following result:

0.2352 gram of the salt gave 0.1645 gram $PbSO_4$.

	Calculated for $C_{12}H_6O_2O_2Pb$.	Calculated for $C_{12}H_5O_2OHO_2Pb$.	Found.
Pb	49.17	47.39	47.76

This result shows that the oxidizing agent, which intro-

duces the additional hydroxyl, is not the oxygen of the air, but the orthoquinone itself, and this view is confirmed by the fact that the chloroform solution, from which the black compound has separated, contains brown substances probably formed from the orthoquinone in oxidizing the insoluble product, but which were so unmanageable that we were unable to determine their composition.

We would add here two analyses made by H. A. Torrey some years ago in this laboratory of a substance agreeing with our black compound in its properties, which he had prepared by the electrolytic oxidation of pyrocatechin. They gave the following results :

I. 0.1275 gram substance gave, on combustion, 0.2940 gram CO_2 and 0.0436 gram H_2O.

II. 0.0608 gram substance gave 0.1401 gram CO_2 and 0.0230 gram H_2O.

	Calculated for $C_{12}H_8O_2(OH)_2$.	Found. I.	II.
C	62.07	62.88	62.85
H	3.45	3.80	4.20

The substance is obviously the same as that previously analyzed, although not so pure.

We have, therefore, four analyses of three samples of this substance prepared or purified in different ways, and, as these agree, there can be no doubt that the black alteration-product of the orthoquinone is a definite compound, and has the composition $C_{12}H_8O_5$.

Properties of the Black Alteration-Product of Orthobenzoquinone (*Orthodioxyphenyloxyorthoquinone*,[1] $C_6H_3(OH)_2C_6H_3(OH)O_2$).– It forms an almost black amorphous powder, which does not melt, but decomposes gradually at temperatures above 170°. It is easily soluble in cold alcohol, ether, or glacial acetic acid; insoluble in benzol or chloroform, whether cold or hot. Strong acids have no apparent action on it, but alkalies dissolve it.

The following experiments were undertaken to determine the constitution of the black alteration-product.

[1] This name and formula for the substance are established by the work described later in this paper.

Reduction of the Alteration-Product.

The formula of the substance $C_{12}H_8O_5$ indicates that it contains two benzol rings, and these may either be united directly, forming a diphenyl compound, or they may be united by 2 atoms of oxygen, forming a substituted pyrocatechin ether $[C_6H_3OH]O_2[C_6H_3(OH)_2]$. The diphenyl formula, $(HO)O_2H_2C_6—C_6H_3(OH_2)$, is rendered probable by the formation of the dinaphthyldiquinhydrone[1] under somewhat similar circumstances from β-naphthoquinone, which has been proved to be a dinaphthyl compound;[2] the pyrocatechin-ether formula, on the other hand, is in harmony with a derivative of tetrabromorthoquinone, which is described later in this paper. Reduction seemed the easiest way to decide between these formulas, as the ether should be split into pyrocatechin and a trioxybenzol, while the diphenyl product would be reduced without splitting apart the two benzol rings. Upon treating the black alteration-product with sodium amalgam and water in an atmosphere of carbonic dioxide for several days, an uninviting black solid was obtained on acidification, which was soaked in water, and this water, as well as the acidified filtrate from the reduction extracted with ether, but not a trace of pyrocatechin was obtained. As the bromether, which we have obtained in another part of our work, gives a large quantity of pyrocatechin by this treatment, we infer that the black alteration-product is a diphenyl derivative.

Action of Benzoyl Chloride on the Black Alteration-Product.

Half a gram of this substance was dissolved in 10 cc. of a solution of potassic hydrate (1 : 5), and to the warm solution benzoyl chloride was added drop by drop, until the product of the reaction rose to the surface as an oily mass, leaving the liquid clear. This was then treated with sodic hydrate, in which it did not dissolve, and thoroughly washed with water. The tarry mass thus obtained was dissolved in chloroform, the solution filtered, and the filtrate mixed with an excess of alcohol, which precipitated out the substance. After drying *in vacuo* it was analyzed, with the following result :

[1] Ann. Chem. (Liebig), 194, 205.
[2] *Ibid.*, 206; Korn : Ber. d. chem. Ges., 17, 3030.

0.2210 gram substance gave, on combustion, 0.5933 gram CO_2 and 0.0744[1] gram H_2O.

	Calculated for $C_{12}H_6O_2(OCOC_6H_5)_2$.	Calculated for $C_{12}H_5O_2(OCOC_6H_5)_3$.	Found.
C	70.91	72.79	73.21
H	3.64	3.68	3.74

The substance is therefore a tribenzoyl compound, and the original black body must have contained three hydroxyl groups. This *benzoxyorthoquinoorthodibenzoxydiphenyl*,

$$C_6H_3(OCOC_6H_5)O_2C_6H_3(OCOC_6H_5)_2,$$[2]

forms a light-yellow, amorphous powder without a definite melting-point. It is easily soluble in chloroform; insoluble in alcohol or water. Alkalies do not dissolve it.

The fact that only three benzoyl groups are taken up by the black alteration-product indicates that two of its five atoms of oxygen do not form part of hydroxyl groups; from the formation of the substance these two atoms of oxygen must either belong to a quinone or be the connecting atoms of a pyrocatechin ether, and, as our work on the reduction of the alteration-product has shown that it is probable they are not pyrocatechin-ether oxygen atoms, there can be little doubt that they occur in the quinone configuration, which indeed was the more probable supposition of the two. We tried to confirm this inference by the formation of hydrazones both from the original black alteration-product and its benzoyl derivative, but without satisfactory results. When phenylhydrazine in excess was added to a solution of 0.5 gram of the black alteration body dissolved in 10 cc. of alcohol, the dark, blackish color of the solution was discharged, and on pouring the product into acidified water a golden-yellow precipitate was formed; but an analysis of the substance gave 6.39 per cent of nitrogen, whereas the most probable formula, $C_{12}H_6O_4NNHC_6H_5$, requires 8.70 per cent of nitrogen. The tribenzoyl derivative of the black substance was dissolved in chloroform and boiled with an excess of phenylhydrazine for several minutes; a new compound was formed, which was

[1] A little water was lost in this analysis.

[2] The distribution of the benzoxy groups in this substance has not been determined.

obtained by allowing the chloroform to evaporate spontaneously, treating with an acid to remove the excess of phenylhydrazine, dissolving the residue in cold alcohol, and precipitating the substance from this solution with water. After drying *in vacuo* it was analyzed and 3.19 per cent of nitrogen found instead of 4.42 per cent of nitrogen required by the formula of the hydrazone,

$$C_{12}H_5O(NNHC_6H_5)(OCOC_6H_5)_3.$$

It is evident from these results that phenylhydrazine acts on both of these substances, and that the product in each case contains nitrogen. The results, therefore, as far as they go, confirm our inference that there are two quinone atoms of oxygen in the black substance, but they are of little value, because the exceedingly unmanageable nature of both of these substances prevented us from purifying them sufficiently to determine their composition with certainty.

The work just described establishes the following points with tolerable certainty. The black alteration-product is a diphenyl compound and contains three hydroxyl groups and an orthoquinone group ; it may therefore be called orthodioxyphenyloxyorthoquinone, and receive the formula

$$C_6H_3(OH)_2C_6H_2(OH)O_2,$$

although the three hydroxyl groups may be attached to the same benzol ring, as we have not determined the position of the third hydroxyl experimentally.

EXPERIMENTS WITH THE SOLUTION OF ORTHOBENZOQUINONE.

Action of Hydrochloric Acid on the Solution of Orthobenzoquinone.

Dry hydrochloric acid gas was passed through a fresh chloroform solution of orthoquinone (prepared from iodine and the lead salt of pyrocatechin) until it fumed strongly. After filtering out a slight tarry precipitate, a large part of the chloroform was recovered by distillation, and the concentrated solution thus obtained allowed to stand over night in an open vessel. The residue, which was usually oily, was heated on the steam-bath to drive off the last traces of the solvent and a

slight impurity of iodine, and then extracted with a hot mixture of 3 parts chloroform with 1 of ligroin, which left behind a large quantity of a black oil. The solution became milky, on standing, and deposited an oily substance, followed, when it had cooled, by the formation of crystals. As soon as these crystals began to appear the clear solution was decanted from the oil and allowed to crystallize in a separate vessel. The residual oils, by a similar treatment with chloroform and ligroin, yielded an additional amount of the crystals. The crystals were dissolved in benzol and treated with bone-black, after which they were purified by repeated crystallizations from the mixture of chloroform and ligroin. They showed the melting-point 84° to 85°, which was not quite constant, indicating that the substance was not perfectly pure; but in spite of this it was dried *in vacuo*, and analyzed with the following result:

0.2005 gram substance gave, by the method of Carius, 0.1865 gram of AgCl.

	Calculated for $C_4H_3Cl(OH)_2$.	Found.
Cl	24.57	23.00

This result indicates that the body is monochlorpyrocatechin, but that it contains some pyrocatechin, as would be expected if the reaction ran in the same way as that of hydrochloric acid on parabenzoquinone, since Wichelhaus[1] has shown that in this case hydroquinone and chlorine are formed in the first instance, and that the substitution compounds, which form the final product, are made by the action of the chlorine on the hydroquinone. We have not attempted to purify the chlorpyrocatechin more thoroughly, as much time and labor would be necessary to obtain sufficient material for this purpose, and the formation of chlorpyrocatechin under these conditions is confirmed by the following analysis of the lead salt, made by adding plumbic acetate to an aqueous solution of the product of the reaction of hydrochloric acid on the solution of orthoquinone.

0.3867 gram salt gave 0.3306 gram of plumbic sulphate.

[1] Ber. d. chem. Ges., **12**, 1504.

	Calculated for $C_6H_3ClO_2Pb$.	Found.
Pb	58.98	58.55

The monochlorpyrocatechin in the slightly impure state in which we obtained it crystallized in white pearly plates, which are easily soluble in water, alcohol, ether, benzol, chloroform, or acetone; insoluble in ligroin. With an aqueous solution of plumbic acetate it gives a lead salt. It blackens quickly if exposed to the air after treatment with an alkali. The melting-point observed by us is, of course, of no value on account of the presence of the impurity of pyrocatechin.

Behavior of the Solution of Orthobenzoquinone with Reducing Agents.

Ammonic Sulphide.—Some of the solution of orthoquinone in chloroform was shaken with about one-third of its volume of the ordinary laboratory solution of ammonic sulphide. The red color of the orthoquinone disappeared, and the aqueous solution took on a dark color. The two liquids were separated by means of a drop funnel, and the chloroform was extracted twice with water, the extracts being added to the ammonic sulphide solution at first obtained. The mixed aqueous portion was then heated on the steam-bath, acidified with hydrochloric acid, allowed to stand until the precipitated sulphur had settled, filtered, and the clear, dark-colored filtrate extracted with ether. The residue, left on the evaporation of the ether, was recrystallized twice from benzol, when it was found to melt constant at 103° to 104°, and to show all the other properties of pyrocatechin. In order to be certain that the pyrocatechin, detected in the product from the action of ammonic sulphide on the orthoquinone solution, was formed from the orthoquinone, it was necessary to prove that this solution contained no free pyrocatechin; for this purpose a small amount of it, taken before the reduction, was shaken with water, the water evaporated, and the residue extracted with benzol; the benzol extract was evaporated to dryness, the very slight residue dissolved in water, and tested with plumbic acetate, when it gave no precipitate, showing that no free pyrocatechin was contained in the chloroform solution.

Action of Sulphurous Dioxide.—Dry sulphurous dioxide was passed through the chloroform solution of orthoquinone until it was saturated; the principal product was a black unmanageable precipitate, probably a compound of orthoquinone and pyrocatechin corresponding to quinhydrone; but the filtrate from this left, on evaporation, crystals which were recognized as pyrocatechin by their properties and the formation of the lead salt.

Action of Bromine on the Solution of Orthobenzoquinone.

An excess of bromine was added to the solution of orthoquinone in chloroform, the chloroform allowed to evaporate spontaneously, and the crystalline residue, after being heated gently to drive off the excess of bromine, was spread on unglazed porcelain to remove oily impurities. After recrystallization from benzol it showed the constant melting-point 191°, which is near enough to 192° to 193°, that given by Zincke[1] for tetrabrompyrocatechin, to leave no doubt as to the nature of the substance. For greater certainty the substance was analyzed with the following results:

I. 0.1835 gram substance gave, by the method of Carius, 0.3210 gram AgBr.

II. 0.1509 gram substance gave 0.2637 gram AgBr.

	Calculated for $C_6Br_4(OH)_2$.	Found. I.	Found. II.
Br	75.11	74.44	74.39

These numbers are sufficiently near to show that the product of the action of bromine on the orthobenzoquinone is tetrabrompyrocatechin.

Behavior of the Solution of Orthobenzoquinone with Benzolsulphinic Acid.

The chloroform solution of orthoquinone was added drop by drop to a solution of benzolsulphinic acid,[2] also in chloroform, until the color began to disappear less rapidly and the solution of the sulphinic acid had assumed a decided reddish tint.

[1] Ber. d. chem. Ges., **20**, 1777.

[2] If the conditions were reversed, and the solution of benzolsulphinic acid was added to the solution of orthoquinone, none of the desired sulphone was obtained; we ascribe this difference in behavior to the oxidation of the sulphinic acid by the excess of orthoquinone.

After standing over night the liquid was filtered, the filtrate evaporated to dryness, and the residue allowed to solidify. The solid residue was next treated with hot benzol, which dissolved all but a slight black residue. On allowing the benzol solution to evaporate, a crystalline substance was obtained, which was purified by crystallization with the aid of bone-black at first from water mixed with a little alcohol, finally from water alone, until it showed the constant melting-point 153°, when it was dried at 100° and analyzed with the following results:

I. 0.2353 gram substance gave, on combustion, 0.4931 gram CO_2 and 0.0862 gram H_2O.

II. 0.1454 gram substance gave, by the method of Carius, 0.1418 gram $BaSO_4$.

	Calculated for $C_6H_3(OH_2)SO_2C_6H_5$.	Found. I.	Found. II.
C	57.60	57.14	....
H	4.00	4.07	....
S	12.80	....	13.39

As this body must be a substituted pyrocatechin it should give a lead salt, and upon trying it with a solution of plumbic acetate we obtained one, which was analyzed with the following result:

0.2601 gram substance gave 0.1729 gram $PbSO_4$.

	Calculated for $C_6H_3O_2PbSO_2C_6H_5$.	Found.
Pb	45.50	45.39

There can be no doubt, therefore, that the substance is a pyrocatechinsulphone or orthodioxydiphenylsulphone.

Properties of Orthodioxydiphenylsulphone, $C_6H_3(OH)_2SO_2C_6H_5$. —It crystallizes from alcohol and water in short, thick, well-formed, white prisms terminated by two planes at an obtuse angle to each other. It contains no water of crystallization and melts at 153°. It is easily soluble in alcohol, ether, chloroform, or glacial acetic acid; very slightly soluble in cold water or benzol, freely soluble in either of these liquids when hot; essentially insoluble in ligroin, either hot or cold. Alkalies dissolve it with a yellow color. Ferric chloride gives a bluish-green color with it, which changes to red on the addi-

tion of sodic carbonate. As has been already mentioned, its aqueous solution gives a precipitate with plumbic acetate.

This substance has the same composition as the orthodioxydiphenylsulphone made by Hinsberg and Himmelschein[1] by oxidizing pyrocatechin in presence of benzolsulphinic acid, and we should expect that the two bodies would be identical, but, strangely enough, they seem to be isomers, since Hinsberg and Himmelschein's compound contains water of crystallization and melts in presence of this at 117°; when dried in the steam-oven, at 143° to 145°; when previously fused in the air, at 164°; whereas, our substance contains no water, and melts at 153°, whether dried at ordinary temperatures or by previous fusion. We made five attempts to prepare their compound according to Hinsberg and Himmelschein, but did not succeed in finding the conditions under which it is formed, which must lie within very narrow limits; and, as in doing this we had devoted more time to the subject than we could afford, we were obliged to abandon our intention of making a comparative study of the two compounds.

Action of Aniline on the Solution of Orthobenzoquinone.

The solution of orthoquinone in chloroform was heated with an excess of aniline for five minutes on the steam-bath; the chloroform was then allowed to evaporate, and the residue, after having been freed from aniline by treatment with hydrochloric acid and washing with water, was purified by recrystallization from a mixture of two parts of alcohol to one of benzol, until it showed the constant melting-point 203°, when it was dried at 100° and analyzed with the following result:

0.2909 gram substance gave 28.2 cc. N at 22° and 774 mm.

	Calculated for $C_6H_2(C_6H_5NH)_2C_6H_5NO$.	Found.
N	11.51	11.27

The substance is therefore a dianilinoquinoneanil. When the aqueous wash-waters obtained in the preparation of this substance were extracted with ether pyrocatechin was obtained, recognized by its odor and lead salt.

[1] Ber. d. chem. Ges., 29, 2025.

Properties of the Dianilinoquinoneanil, $C_6H_2(C_6H_4NH)_2C_6H_3NO$.—Crystallized from alcohol and benzol it forms bronze-colored small needles, melting at 203°, although they begin to draw together somewhat at 198°. The melting-point of this substance is identical with that (202° to 203°) given by Zincke and Hagen[1] for the dianilinoquinoneanil made from paraquinone by the action of aniline and glacial acetic acid, and as a comparison of the two substances showed they crystallized in the same form, there can be no doubt of their identity. The formation of a paraquinone derivative from our orthoquinone has been already explained in the introduction to this paper.

In the hope of obtaining a phenazine the solution of orthoquinone was treated with orthophenylenediamine; a reaction took place, the principal products of which consisted of uninviting black substances and pyrocatechin recognized by the formation of its lead salt. From the appearance of the pyrocatechin we inferred that the reaction consisted principally in the oxidation of the diamine by the orthoquinone, and as, even after trying the experiment under several varying conditions, no more promising results were obtained this line of work was abandoned. Phenol also gave, with the solution of orthoquinone, such an uninviting product that we did not attempt to study it. Sodic hydrate gives, with the orthoquinone solution, a green coloration similar to that obtained by the action of sodic hydrate on tetrabromorthoquinone.

DERIVATIVES OF TETRABROMORTHOBENZOQUINONE.

The tetrabromorthoquinone used in this work was prepared as follows: 20 grams of pyrocatechin were dissolved in 50 cc. of glacial acetic acid and 37 cc. of bromine added gradually from a burette. The mixture was allowed to stand over night, after which the product was purified by recrystallization from 200 cc. of glacial acetic acid. In this way 40 grams of pyrocatechin yielded 118 to 126 grams of recrystallized tetrabrompyrocatechin; that is, between 75 and 80 per cent of the theoretical yield. To convert this tetrabrompyrocatechin into tetrabromorthoquinone 30 grams of it were dissolved in 300

[1] Ber. d. chem. Ges., 18, 787.

cc. of glacial acetic acid, by heating on the water-bath; the solution was then cooled to 16°, or until the glacial acetic acid began to solidify, and 11 grams of fuming nitric acid (sp. gr. 1.5) diluted with 60 cc. of glacial acetic acid added rapidly, the mixture being kept cool and stirred vigorously during the addition; after standing for five minutes 300 cc. of water were added and stirred in thoroughly. If the process had run successfully, the tetrabromorthoquinone settled to the bottom in a glistening mass of dark-red crystals, which were filtered off and dried. The product thus obtained melted at 145° to 147° instead of 150° to 151°, but was pure enough for our work, which was fortunate, as recrystallization from glacial acetic acid is attended by a great loss of material. Thirty grams of tetrabrompyrocatechin gave 18 grams of tetrabromorthoquinone, which amounts to about 60 per cent of the theoretical yield.

As has just been stated, the crystallization of tetrabromorthobenzoquinone from glacial acetic acid cannot be effected without considerable loss, which we found was due to the conversion of the tetrabromorthoquinone into two new bodies, one of which was red, the other white.[1] A more careful study of the conditions under which the red body was formed showed us that it was produced by the action of the orthoquinone with tetrabrompyrocatechin, either existing as an impurity in our tetrabromorthoquinone or formed from it by reduction. After this the study of this red product was carried on with comparatively little difficulty.

Preparation of Hexabromorthoquinopyrocatechin Ether, $C_{12}Br_6O_4$.

Eleven grams of tetrabromorthoquinone and 10 grams of tetrabrompyrocatechin were dissolved in 470 cc. of glacial acetic acid by heating the mixture on the steam-bath; 180 cc. of water were then added, which produced no immediate precipitate, and the mixture allowed to stand in a warm place for twenty-four hours. During this time a red precipitate was formed, which was filtered out and washed with hot alcohol to

[1] Zincke (Ber. d. chem. Ges., **30**, 1777) observed that acetic acid acted on tetrabromorthoquinone but did not isolate the products of the action.

remove unaltered tetrabromorthoquinone and pyrocatechin. In this way 10.7 grams were obtained; that is, somewhat over 60 per cent of the theoretical yield. The purification of the substance offered at first some difficulty because it was insoluble in all the common solvents, but later we found that it dissolved to a limited extent in hot nitrobenzol, and proceeded as follows: Two grams of the crude red body were dissolved in 150 cc. of nitrobenzol by heating the mixture on the steam-bath (at higher temperatures more of the substance will dissolve, but the solution is attended with decomposition). Upon cooling, the solution deposited about 0.7 gram of crystals, which were submitted to a second similar crystallization from nitrobenzol at 100°, after which the product was extracted several times with hot alcohol to remove adhering nitrobenzol, dried at 100°, and analyzed. As the substance does not melt, we had no means of determining whether this treatment had been an efficient purification.

I. 0.1809 gram substance gave, on combustion, 0.1374 gram CO_2 and 0.038 gram H_2O.

II. 0.1008 gram substance gave, by the method of Carius, 0.1637 gram AgBr.

III. 0.1129 gram substance gave 0.1843 gram AgBr.

	Calculated for $C_{12}Br_4O_4$.	Found. I.	II.	III.
C	20.93	20.71	....	....
H	0.00	0.23	....	....
Br	69.76	....	69.13	69.49

Properties of Hexabromorthoquinopyrocatechin Ether.—The substance crystallizes from warm nitrobenzol in short, slender prisms of a pure vermilion-red color; it does not melt and is insoluble in all the common solvents; nitrobenzol dissolves it especially when warm, but if the solution is heated above 100° decomposition sets in, as shown by a change of color. The ordinary strong acids have no effect on it in the cold, but fuming nitric acid dissolves it with decomposition; alkalies do not dissolve it, but the substance turns black after standing with an alkali for a short time. The red color of the substance indicates that it contains two orthoquinone oxygen

atoms, and this view is confirmed by its behavior with hydrochloric acid and reducing agents described later.

The red substance is probably formed from tetrabrompyrocatechin and tetrabromorthoquinone by the following reaction:

$$C_6Br_4(OH)_2 + C_6Br_4O_2 = C_6Br_4O_2C_6Br_2O_2 + 2HBr.$$

To test this a new preparation was made as described above, and after the mixture had stood twenty-four hours it was diluted with five times its volume of water, the reddish-white precipitate formed filtered out, the aqueous filtrate acidified with nitric acid, and treated with argentic nitrate, when a heavy precipitate of argentic bromide was thrown down, showing the presence of hydrobromic acid among the products of the reaction. It was also found that the best yield was obtained when the two reagents were used in the proportion of equal molecules, as required by the reaction. The best solvent to be used in the preparation was glacial acetic acid and water, as already described, but the red body was also formed in dilute alcohol (the proportions used were 0.5 gram of each reagent, 40 cc. of alcohol, and 10 cc. of water). On the other hand, no reaction was observed when the solvent was ether or chloroform. One gram of each of the reagents was dissolved in 50 cc. of ether (care was taken that the substances were free from even a trace of acetic acid), and allowed to stand twenty-four hours. As no precipitate had formed, the ether was allowed to evaporate spontaneously, when a reddish-white residue was left, which looked like a mixture of the unaltered reagents, and dissolved completely in hot chloroform. This showed that none of the hexabromorthoquinopyrocatechin ether had been formed, as it is insoluble in chloroform. Another portion of the residue from the ethereal solution was dissolved in glacial acetic acid and slightly diluted, when a copious deposit of the red body appeared on standing. The fact that we observed no action when the tetrabromorthoquinone and tetrabrompyrocatechin were mixed in ether is strange, since Zincke[1] states that by the action of these two bodies in ether or benzol he obtained black shining needles,

[1] Ber. d. chem. Ges., **20**, 1778.

which changed color at 110° and formed a brownish liquid. We are unable to explain this difference in the results of the experiments, but hope that future work may lead us to the conditions necessary for preparing the black substance.

If the substance is formed by the reaction given above, it is probable that the two benzol rings are connected by two of the atoms of oxygen; but this is not necessarily the case, as the product might also be a derivative of diphenyl, in which both rings contain orthoquinone groups. To settle the mode of union of the two benzol rings, we submitted the substance to reduction with sodium amalgam, as follows: Ten grams of the red substance were covered with water in a flask, from which all the air was excluded by a stream of carbonic dioxide, 3 per cent sodium amalgam was then added in large excess, and the reaction was allowed to run at ordinary temperatures in the atmosphere of carbonic dioxide for several days. At the end of this time the red substance had been converted principally into a purplish-white body, which seemed to resist the further action of the sodium amalgam; it was, therefore, filtered out and washed with dilute acid and alcohol; the aqueous filtrate from this substance gave no precipitate on acidification, but on subsequent extraction with ether we obtained from the extract a considerable quantity of a white residue, which, after several crystallizations from benzol, gave the melting-point 100° instead of 104°, the true melting-point of pyrocatechin; from the form of its crystals, however, and as it gave the lead salt and the characteristic color with ferric chloride, there can be no doubt that it was pyrocatechin. As has been stated, the principal product of this reduction was the purplish-white insoluble substance, the weight of which amounted to 6 grams from 10 grams of the red body; it was obvious, therefore, that no safe inference in regard to the constitution of the red substance could be drawn from the appearance of this small proportion of pyrocatechin. Accordingly, in the hope of increasing our yield of pyrocatechin, this purplish-white product was submitted to reduction with sodium amalgam under the conditions used in its forma-

tion, the action in this case being allowed to continue for a week, but, as we had reason to expect from our observations in our first reduction, the substance remained essentially unaltered, not more than a trace of pyrocatechin being formed. Meanwhile, we had discovered that the purplish-white product was converted by nitric acid into the original red substance, and, therefore, we oxidized the unaltered body from the last reduction, and on reducing this again with sodium amalgam, obtained a fresh amount of pyrocatechin with the purplish-white product again. By repeating these alternate oxidations and reductions we have succeeded in converting a sample of the red substance completely into pyrocatechin, a result which, it seems to us, proves that this red body is a pyrocatechin ether and not a diphenyl derivative.

The purplish-white product of the reduction of hexabromorthoquinopyrocatechin ether by sodium amalgam, mentioned frequently in the preceding paragraph, proved to have the same solubilities as the mother substance; that is, it was insoluble in all the common solvents except nitrobenzol. It was accordingly recrystallized three times from boiling nitrobenzol, when, as it does not have a definite melting-point, it was assumed to be pure. After extraction with alcohol, to remove adhering nitrobenzol, it was dried at 100° and analyzed with the following result:

0.1215 gram substance gave, by the method of Carius, 0.1974 gram AgBr.

	Calculated for $C_{12}Br_4(OH)_2O_2$.	Found.
Br	69.56	69.16

Properties.—The substance crystallizes from hot nitrobenzol in very small chocolate-brown crystals, which appear to be short, rather blunt, needles. As obtained from reduction, it has a purplish-white color and a characteristic silky luster. It does not melt at 300°. It is insoluble in all the common solvents except nitrobenzol. An aqueous solution of sodic hydrate does not dissolve it; fuming nitric acid converts it back into the red substance from which it was made, as is proved by the following experiment:

Three grams of the chocolate-colored crystals of the reduction-product were mixed with 20 cc. of glacial acetic acid, and 5 cc. of fuming nitric acid were added. The solid immediately turned red, and, after the mixture had been thoroughly stirred, it was poured into water and washed. The oxidation was then repeated in the same way, and the dried product was found to weigh 3 grams; the conversion from the chocolate-colored substance to the red body, therefore, takes place quantitatively. The red product was recrystallized from warm nitrobenzol, freed from the excess of nitrobenzol with alcohol, dried at 100°, and analyzed with the following result:

0.1317 gram substance gave, by the method of Carius, 0.2140 gram AgBr.

	Calculated for $C_{12}Br_6O_4$.	Found.
Br	69.76	69.15

There can be no doubt that this substance is the hexabromorthoquinopyrocatechin ether described above.

As to the formula of the chocolate-colored product of the reduction there is a certain amount of doubt. Our analysis shows only that its composition does not differ to a marked extent from that of the red mother-substance. Its formation by reduction and its conversion to the original body by nitric acid would indicate that it was the hydroxyl compound corresponding to the red quinone, but, on the other hand, its insolubility in sodic hydrate is hard to reconcile with this view. As this may be due, however, to the very slight solubility of the substance in all solvents, which might prevent the sodic hydrate from coming sufficiently in contact with it to react, we are inclined to consider that it is the hexabromorthodioxypyrocatechin ether, and to assign it provisionally the formula $C_{12}Br_6O_2(OH)_2$. We hope that the study of this substance may be finished in this laboratory in the near future.

Our attempts to decompose the hexabromorthoquinopyrocatechin ether with sulphuric acid led to no result, as no action was observed even after boiling it for several hours with sulphuric acid of 1.44 or even 1.6 sp. gr.; but hydrochloric acid reacted upon it, as is shown by the following experiment: 5 grams of the red body were sealed in a tube with 25

cc. of strong hydrochloric acid and heated from 160° to 175° for five hours ; the product, after being washed with water and alcohol, showed a strong resemblance to the purplish-white body obtained by the reduction with sodium amalgam. On treating it with fuming nitric acid diluted with glacial acetic acid it turned red at once, so that there can be little doubt of the identity of the two substances. This observation can be satisfactorily explained on the theory already adopted, that the purplish-white substance is the dihydroxy derivative from the red orthoquinone body, as then this action is the familiar reduction of quinone oxygen by hydrochloric acid. This theory is still further supported by the reduction of tetrabromorthoquinone to the purplish-white body by tribrompyrogallol described in the next section.

Behavior of Tetrabromorthoquinone with Tribromresorcin.

After we had found, as just described, that tetrabromorthoquinone reacted with tetrabrompyrocatechin, it became of interest to try the action of the tetrabromorthoquinone with other diatomic phenols, and, as we found that unsubstituted phenols of this class reduced the quinone,—pyrocatechin, for instance, reducing it completely to tetrabrompyrocatechin,—we turned our attention to the bromphenols. Of these, tetrabromhydroquinone in alcoholic solution acted only as a reducing agent, giving bromanil and tetrabrompyrocatechin. Tribrompyrogallol also acted only as a reducing agent, giving tetrabrompyrocatechin, which combined with unreduced tetrabromorthoquinone to give the hexabromorthoquinopyrocatechin ether, and this was converted by further action of the tribrompyrogallol into its purplish-white reduction-product. With tribromresorcin, on the other hand, a new compound was obtained.

Eight and four-tenths grams of tetrabromorthoquinone and 7 grams[1] of tribromresorcin[2] were dissolved with the aid of

[1] The two reagents were used in the proportion of equal molecules, whereas the analysis of the product showed that 2 molecules of the resorcin should have been taken for each molecule of the quinone.

[2] The tribromresorcin was prepared by the method of Benedikt (Monatsh. f. Chem., 4, 227) by mixing the calculated amount of bromine with resorcin dissolved in glacial acetic acid. The product was purified by crystallization from benzol and ligroin.

heat in 600 cc. of glacial acetic acid mixed with 400 cc. of water, and allowed to stand for twenty-four hours. At the end of this time a dingy pink precipitate had formed, which was filtered out, washed, and recrystallized from benzol until it showed the constant melting-point 217°, when it was dried at 100°, and analyzed with the following result:

I. 0.1389 gram substance gave, by the method of Carius, 0.2173 gram AgBr.

II. 0.1370 gram substance gave, by the method of Carius, 0.2144 gram AgBr.

	Calculated for $(C_6Br_3HOHO)_2C_6Br_2O_2$.	Found. I.	II.
Br	66.94	66.58	66.61

The substance, therefore, is evidently formed by the union of 2 molecules of the resorcin with 1 of the quinone with elimination of 2 molecules of hydrobromic acid, and may be called the ditribrommetoxyphenyldibromorthoquinophenylene ether.

Properties.—It crystallizes from benzol in slender lemon-yellow prisms with square ends and melts at 217°. It is soluble in ether, slightly soluble in cold alcohol or chloroform, easily soluble in either of these solvents when hot; nearly insoluble in cold benzol, much more soluble in hot benzol, which is the best solvent for it. It does not dissolve in sodic hydrate, which throws some doubt on the formula we have ascribed to it, as this contains two hydroxyl groups.

Action of Glacial Acetic Acid on the Tetrabromorthoquinone.

As has been already stated, tetrabromorthoquinone, when crystallized from glacial acetic acid, is partially converted into a white substance,[1] which we found it convenient to prepare as follows: 10 grams of tetrabromorthoquinone were dissolved in 80 cc. of glacial acetic acid and the solution slowly evaporated to dryness on the steam-bath, the reddish-white residue was moistened with 10 cc. glacial acetic acid and the slow evaporation on the steam-bath repeated, in order to act on any

[1] Zincke (Ber. d. chem. Ges., 20, 1777) converted tetrabromorthoquinone, into a white substance by crystallizing it from a mixture of ether and ligroin. On repeating the experiment we did not succeed in finding the conditions under which the white product is formed.

tetrabromorthoquinone which might have escaped the previous reaction; the residue was then extracted with 200 cc. of hot alcohol and filtered boiling, when the red hexabromorthoquinopyrocatechin ether previously described was left behind, as it is insoluble in alcohol. This substance seemed to be a constant product of the reaction, but not a principal one, as the amount was only about 0.8 gram. The alcoholic solution was allowed to cool and filtered again; then it was diluted with 200 cc. of water, which precipitated out the white product, amounting to from 5 to 6 grams. This was purified by crystallization from glacial acetic acid until it showed the constant melting-point 230°, when it was dried at 100°, and analyzed with the following results:

I. 0.2658 gram substance gave, on combustion, 0.1903 gram CO_2 and 0.0179 gram H_2O.

II. 0.1373 gram substance gave, by the method of Carius, 0.2306 gram AgBr.

III. 0.3015 gram substance gave, on combustion, 0.2090 gram CO_2 and 0.0223 gram H_2O.

IV. 0.1265 gram substance gave 0.2122 gram AgBr.

V. 0.1279 gram substance gave 0.2147 gram AgBr.

VI. 0.1138 gram substance gave 0.1911 gram AgBr.

VII. 0.1229 gram substance gave 0.2074 gram AgBr.

	Found.						
	I.	II.	III.	IV.	V.	VI.	VII.
C	19.53	....	18.90	....	....	....	....
H	0.75	....	0.82	....	....	....	....
Br	....	71.45	....	71.39	71.44	71.48	71.83

Of these analyses I and II were of samples prepared and purified as described; III to VII were of specimens prepared earlier in our work, and in some cases purified by slightly different, and perhaps less effective, methods.

Two determinations of the molecular weight were made by the method of freezing, the solvent being benzol.

I. 0.262 gram substance dissolved in 16.58 grams benzol produced a depression of 0°.099.

II. 0.594 gram substance in 16.58 grams benzol produced a depression of 0°.219.

	I.	II.
Molecular weight	782	802

The most probable formula to be derived from these data is $C_{14}H_3Br_5O_5$, formed by the union of 2 molecules of tetrabromorthoquinone with 1 of acetic acid, 1 molecule of water being eliminated. The results, however, agree almost as well with $C_{14}Br_6O_5$, although the percentage of hydrogen found is high for a substance which is free from this element. A compound with the formula $C_{14}Br_8O_5$ would be formed by the removal of 2 atoms of hydrogen from the preceding compound, a reaction which might easily be brought about by the oxidizing action of a portion of the tetrabromorthoquinone; the tetrabrompyrocatechin thus formed in turn acting on the unaltered quinone would give the red body which, as already stated, is always produced with the white substance; but it should be remembered that the quantity of the red body formed is far below that which would be expected from such a reaction.

	Calculated for $C_{14}H_3Br_5O_5$.	Calculated for $C_{14}Br_8O_5$.	Found. I.	Found. II.
C	18.88	18.92	19.53	....
H	0.22	....	0.75	....
Br	71.95	72.07	....	71.45
Mol. wt.	890	888	782	802

It is obvious that the decision can be made between these formulas only by the chemical study of the substance, but, unfortunately, we have not succeeded as yet in decomposing it by any of the reagents we have tried, so that we must leave this question undecided for the present, with the statement that we consider the formula $C_{14}H_3Br_5O_5$ the most probable. The study of the substance will be continued in this laboratory next year.

Properties of the Substance, $C_{14}H_3Br_5O_5$.—When crystallized from glacial acetic acid it forms small, almost square rhombic plates with a pearly luster, which melt at 230°. It is easily soluble in ether, benzol, chloroform, acetone, or ethyl acetate; almost insoluble in glacial acetic acid, but its solubility is increased by heat, as the boiling acid takes up from 2 to 3 per cent of the substance. Its solubility in ethyl alcohol is similar to that in glacial acetic acid; curiously enough, when first formed, the crude mass is rather freely soluble in alcohol, but, as the purification continues, it becomes less and less so,

until, when pure, it is nearly insoluble in cold alcohol, as already stated. It is essentially insoluble in ligroin or in water, hot or cold. The best solvent for it is glacial acetic acid. None of the strong acids dissolve it when cold; nor does even a hot solution of sodic hydrate show any perceptible action upon it.

The substance is decidedly stable, as is shown by the following experiments, which were tried in the hope of decomposing it into simpler bodies, in order to throw some light on its nature: 0.5 gram of the white substance were treated with sodium amalgam and water in an atmosphere of carbonic dioxide for eight days. At the end of this time the substance was recovered unaltered, as shown by its melting-point. The filtrate was acidified and extracted with ether, but yielded no pyrocatechin. Two-tenths gram of the substance was dissolved in boiling glacial acetic acid and mixed with 5 cc. of fuming nitric acid also diluted with glacial acetic acid; no visible reaction took place, and upon dilution with water the original substance was obtained, as shown by the melting-point. Two-tenths gram was dissolved in cold chloroform and 3 cc. of bromine added; after standing for twenty-four hours the chloroform was evaporated, leaving the original substance, as shown by the melting-point. Two-tenths gram of the substance was dissolved in benzol and an excess of aniline added; after standing for twenty-four hours the benzol and aniline were removed, when the unaltered substance was obtained, as shown by the melting-point. Phenylhydrazine gave a similar negative result. No action could be observed when the substance was treated with an alkaline solution of potassic permanganate, or was boiled with sulphuric acid of sp. gr. 1.44 or 1.6, or heated to 150° in a sealed tube with hydrochloric acid. If it was heated to 250° with hydrochloric acid the compound was completely destroyed, and complete destruction also ensued when it was treated with fuming nitric acid, or a solution of chromic anhydride, or when it was fused with potassic hydrate. In continuing this work next year, renewed attempts will be made to obtain decomposition-products of the substance, and efforts will also be

made to throw light on its constitution by preparing allied compounds.

It should also be mentioned that acetic ester converts tetrabromorthoquinone into tetrabrompyrocatechin, which then forms hexabromorthoquinopyrocatechin ether with unaltered tetrabromorthoquinone. Chloral showed no action with tetrabromorthoquinone even at 100°. The study of the little-known and very reactive tetrabromorthoquinone will be continued in various directions in this laboratory.

CXXV.—ON THE ACTION OF SODIC SULPHITE ON TRIBROMDINITROBENZOL AND TRIBROMTRINITROBENZOL.[1]

By C. Loring Jackson and Richard B. Earle.

In the course of an extended study of the action of various reagents on tribromdinitrobenzol ($Br_3$1.3.5.(NO_2)$_2$2.4.), it became of interest to determine whether this substance could be converted into a sulphonic acid by the method of Strecker,[2] that is, boiling the halogen compound with an aqueous solution of normal sodic sulphite, and experiments in this direction were tried rather early in the work, with negative results. Upon returning to the subject later we did not find any conditions under which an aqueous solution of sodic sulphite acted on tribromdinitrobenzol, but when we substituted alcohol for water as the solvent we obtained a reaction. This, however, took a different direction from that which we had expected, as under these conditions the sodic sulphite acts as a reducing agent, converting the tribromdinitrobenzol into dibromdinitrobenzol by replacing one of the atoms of bromine by hydrogen. The atom of bromine replaced is the one between the two nitro groups, since the dibromdinitrobenzol formed melted at 117°, which is the melting-point of the dibromdinitrobenzol,[3] $Br_2$1.3.(NO_2)$_2$4.6. That the product had this constitution was confirmed by its conversion into the bromanilidodinitrobenzol, which showed the melting-point 157°.[4] Tribromtrinitroben-

[1] Presented to the American Academy of Arts and Sciences, May 9, 1900.

[2] Ann. Chem. (Liebig), 148, 90.

[3] Koerner: Gazz. chim. ital., 1874, 305.

[4] Jackson and Cohoe: This Journal, 26, 5.

zol undergoes a similar reduction with an alcoholic solution of normal sodic sulphite, the product being dibromtrinitrobenzol, which can have only this constitution: $Br_2$1.3.$(NO_2)_2$2.4.6. It is a new substance and melts at 135°.

In the hope of finding an easier method for making this dibromtrinitrobenzol the action of dibromdinitrobenzol ($Br_2$1.3.$(NO_2)_2$4.6) with nitric and sulphuric acids was studied. This gave the desired dibromtrinitrobenzol, but the product was mixed with so large a proportion of tribromdinitrobenzol that the method was not adapted to the preparation of the substance. This tribromdinitrobenzol is a new substance melting at 150°. There can be no doubt that its constitution is $Br_3$1.2.3.$(NO_2)_2$4.6, since it is made by introducing a third atom of bromine into the dibromdinitrobenzol, $Br_2$1.3.$(NO_2)_2$4.6, and, if this occupied the only other vacant place (5), the product would be the common tribromdinitrobenzol, which melts at 192°. The formation of this tribromdinitrobenzol during this reaction is strictly according to the analogy of the behavior of the tribromdinitrobenzol, which, when boiled with a mixture of fuming nitric and sulphuric acids, gives rise to tribromtrinitrobenzol and tetrabromdinitrobenzol.[1]

As neither of the new substances just described can be prepared easily on a large scale, we have confined our work on them to the study of the principal action of sodic ethylate on each. This reaction runs in a normal way, giving styphnic diethyl ether,

$$C_6H(NO_2)_3(OC_2H_5)_2, \quad ((OC_2H_5)_2\text{1.3.}(NO_2)_2\text{4.6.}),$$

with dibromtrinitrobenzol, recognized by its melting-point 121°; and with tribromdinitrobenzol a new bromdinitroresorcinmonoethyl ether melting at 78°. The subject did not promise to be of sufficient interest to make it worth while to study the secondary products of these reactions.

EXPERIMENTAL PART.

Action of Sodic Sulphite in Alcoholic Solution on Tribromdinitrobenzol.

Five grams of symmetrical tribromdinitrobenzol ($Br_3$1.3.5

[1] Jackson and Wing: This JOURNAL, 10, 284.

$(NO_2)_2$2.4) were dissolved in 70 cc. of alcohol mixed with 20 cc. of benzol, 5 grams of normal sodic sulphite added, and the mixture boiled for five hours in a flask with a return condenser. The red liquid thus obtained was filtered from the insoluble portion, evaporated to dryness, and the residue washed with water, until the yellow color was removed. The part insoluble in water was then recrystallized from alcohol with the aid of bone-black, until it showed the constant melting-point 117°. This melting-point indicated that it was Koerner's dibromdinitrobenzol[1] ($Br_2$1.3.$(NO_2)_2$4.6.), and this was confirmed by treating it with aniline in the cold, when it was converted into the bromanilidodinitrobenzol,[2]

$$C_6H_1Br(C_6H_5NH)(NO_2)_2,$$

recognized by its melting-point 157°. For greater certainty the dibromdinitrobenzol was dried at 100° and analyzed with the following results:

I. 0.3277 gram substance gave 24.6 cc. N at 18°.5 and 760.3 mm.

II. 0.3195 gram substance gave, by the method of Carius, 0.3707 gram AgBr.

	Calculated for $C_6H_2Br_2(NO_2)_2$.	Found. I.	II.
N	8.59	8.65	....
Br	49.38	....	49.08

The sodic sulphite, therefore has removed the atom of bromine standing between the two nitro groups in the tribromdinitrobenzol and replaced it by hydrogen.

That this was not the only action of the sodic sulphite was shown by the marked yellow color of the products of the reaction. The yellow substance was soluble in water, but, in spite of its strong color, was present in such small quantity that we could not isolate it from the other substances soluble in water, which consisted of sodic bromide and unaltered sodic sulphite. It was undoubtedly the sodium salt of a phenol formed by a secondary reaction.

[1] Gazz. chim. ital., 1874, 305.

[2] Jackson and Cohoe: This JOURNAL, **26**, 5.

Action of Sodic Sulphite in Alcoholic Solution on Tribromtrinitrobenzol.

Ten grams of symmetrical tribromtrinitrobenzol ($Br_3$1.3.5.(NO_2)$_3$2.4.6) were dissolved in 120 cc. of common alcohol with the assistance of 30 cc. of benzol, 10 grams of normal sodic sulphite added, and the mixture boiled for four hours in a flask fitted with a return condenser. The reaction seemed to run as in the case of the tribromdinitrobenzol, except that it took place more easily, since the red color appeared more quickly. The red solution was filtered, the filtrate evaporated to dryness, and the residue washed with water, after which it was recrystallized from a mixture of alcohol and benzol with the assistance of bone-black, until it showed the constant melting-point 135°, when it was dried at 100° and analyzed with the following results:

I. 0.2384 gram substance gave 25.1 cc. N at 25° and 753.3 mm.

II. 0.2887 gram substance gave, by the method of Carius, 0.2910 gram AgBr.

	Calculated for $C_6HBr_2(NO_2)_3$.	Found. I.	II.
N	11.36	11.65	....
Br	43.10	....	42.89

The substance is, therefore, dibromtrinitrobenzol ($Br_2$1.3.(NO_2)$_3$2.4.6), formed by the replacement of 1 atom of bromine in the tribromtrinitrobenzol by hydrogen, and the sodic sulphite has behaved like a reducing agent in this case just as it did with the tribromdinitrobenzol.

Properties of Metadibrom-s-trinitrobenzol.—It crystallizes from benzol—or better, a mixture of benzol and ligroin—in broad prisms terminated by two planes at a slightly acute angle to each other, or in slender, blunt-ended prisms, or in rhombic crystals. It has a pale-yellow color with a slight greenish tinge, and melts at 135°. It is freely soluble in benzol or ether; soluble in chloroform, acetone, or cold alcohol; freely soluble in hot alcohol; slightly soluble in hot ligroin; insoluble in water. The best solvent for it is a mixture of alcohol and benzol, or of benzol and ligroin; strong hydrochloric or sulphuric acid has no action on it, either hot or

cold. Strong nitric acid does not dissolve it in the cold, but forms a yellow solution with it when hot, which deposits the unaltered substance on cooling. Sodic hydrate solution gives a pale yellow solution when hot; no perceptible action when cold. Alcoholic sodic hydrate gives a deep red color.

The aqueous wash-waters obtained in the preparation of dibromtrinitrobenzol by this process, although showing a strong red color, contained so little organic matter that we did not succeed in isolating any new compound from them. The residue left on evaporating them consisted chiefly of sodic bromide and unaltered sodic sulphite.

Preparation of Dibromtrinitrobenzol from Dibromdinitrobenzol.

In the hope of finding an easier method of preparing the dibromtrinitrobenzol we next tried to make it from dibromdinitrobenzol. The dibromdinitrobenzol was made by the method of Jackson and Cohoe,[1] which, however, we modified somewhat in converting the bromacetanilide into dibromacetanilide—the monobromacetanilide was mixed with enough glacial acetic acid to convert it into a semi-liquid mass, to which the calculated amount of bromine was added from a burette. It was then warmed on the steam-bath until it was transformed into a clear, dark-red liquid, which was poured into water, filtered, and the precipitate ground in a mortar with a solution of sodic hydrate to remove the excess of bromine. The dibromdinitrobenzol used for our work was recrystallized until it showed the correct melting-point 117°.

To convert the dibromdinitrobenzol into dibromtrinitrobenzol we proceeded as follows: Twenty grams of dibromdinitrobenzol were added to 500 cc. of fuming nitric acid of sp. gr. 1.50 and 200 cc. of sulphuric acid of sp. gr. 1.86, and the mixture was boiled violently for about three hours in a flask closed with a porcelain crucible. Toward the close of the operation a reddish oil separated, after which the process was continued only so long as the liquid boiled freely, since decomposition and darkening of the color resulted from too long-continued boiling. After the mixture had been boiled for a sufficiently long time it was allowed to cool, poured into ice-water, and filtered.

[1] This JOURNAL, 26, 1.

The precipitate was recrystallized from a mixture of alcohol and benzol until it showed a constant melting-point, but as this stood at 150° the substance was not the expected dibromtrinitrobenzol, which melts at 135°. On examining the mother-liquors from this substance, however, we found the dibromtrinitrobenzol, which, after purification by crystallization from a mixture of benzol and ligroin, was recognized by its melting-point 135°, and the following analysis of the substance dried at 100°:

0.2174 gram substance gave, by the method of Carius, 0.2203 gram AgBr.

	Calculated for $C_6HBr_2(NO_2)_3$.	Found.
Br	43.10	43.10

The dibromtrinitrobenzol is therefore formed by this process, but so much of the other product melting at 150° is formed at the same time that this is not a convenient method of preparing it, and the dibromtrinitrobenzol remains a not easily accessible substance.

Tribromdinitrobenzol,

$C_6HBr_3(NO_2)_2$, $(Br_3 1.2.3.(NO_2)_2 4.6.)$.

The substance melting at 150°, prepared by the action of nitric acid and sulphuric acid on dibromdinitrobenzol as described in the preceding section, was dried at 100° and analyzed with the following results:

I. 0.2973 gram substance gave, according to the method of Carius, 0.4138 gram AgBr.

II. 0.2987 gram substance gave 0.4150 gram AgBr.

	Calculated for $C_6HBr_3(NO_2)_2$.	Found.	
		I.	II.
Br	59.26	59.24	59.13

The substance is, therefore, a tribromdinitrobenzol, and its appearance is not unexpected, since J. F. Wing and one of us[1] found that tetrabromdinitrobenzol was always formed during the preparation of tribromtrinitrobenzol from tribromdinitrobenzol. There can be no doubt about the constitution of this tribromdinitrobenzol, because it is made from the dibrom-

[1] This JOURNAL, 10, 284.

dinitrobenzol ($Br_2$1.3.$(NO_2)_2$4.6) by the introduction of an atom of bromine which can enter only in two places—between the nitro groups or between the atoms of bromine. If the substitution takes place between the nitro groups there must be formed symmetrical tribromdinitrobenzol, which melts at 192°; there is left, therefore, for our substance melting at 150° only the constitution $Br_2$1.2.3.$(NO_2)_2$4.6.

Properties of the 1.2.3.Tribrom-4.6.Dinitrobenzol.—Yellowish-white rectangular plates beveled on the sides, when crystallized from a mixture of alcohol and benzol. Melting-point 150°. It is freely soluble in benzol or ether; soluble in chloroform, glacial acetic acid, or acetone; soluble in cold alcohol, freely soluble in hot alcohol; slightly soluble in cold ligroin, soluble in hot; insoluble in water. The best solvent for it is a mixture of alcohol and benzol. Strong hydrochloric or sulphuric acid gives no visible action hot or cold. Strong nitric acid appears not to act in the cold, but dissolves it when hot, depositing the unaltered substance as it cools. A solution of sodic hydrate does not act on it apparently either hot or cold, but in presence of alcohol gives a light yellow color.

Action of Sodic Ethylate on Dibromtrinitrobenzol.

One and a half grams of dibromtrinitrobenzol ($Br_2$1.3.$(NO_2)_2$2.4.6) were dissolved in 15 cc. of benzol and mixed with sodic ethylate in the proportion of 3 molecules of the ethylate to each molecule of the dibrom compound. The sodic ethylate was prepared by adding the calculated amount of sodium to 30 cc. of absolute alcohol. The liquid at once took on an intense red color and became turbid. To make sure of completing the reaction the mixture was allowed to stand for twelve hours at ordinary temperature in a corked flask, after which it was filtered and the filtrate allowed to evaporate spontaneously; the residue was washed with water until the washings were colorless, and then recrystallized from alcohol until it showed a constant melting-point, which was found to be 121°. The melting-point of styphnic ethyl ether,

$$C_6H(OC_2H_5)_2(NO_2)_2 \quad (OC_2H_5)_2\text{1.3.}(NO_2)_2\text{2.4.6},$$

is given as 120°.5, and it is described as forming long plates,

which quickly turn orange-brown in the light; our substance crystallized in prisms connected by their longer sides, and turned brown by exposure to the light. It contained no bromine. There can be no doubt, therefore, that the two bodies are identical, and that this styphnic ether formed by replacing each bromine by an ethoxy group is the principal product of the reaction. It was not, however, the only product of the action of sodic ethylate on dibromtrinitrobenzol, as the reaction product insoluble in the organic solvents, but soluble in water, gave tests for nitrite as well as bromide, and the aqueous washings were colored; but the amount of these secondary products was so small that they could not have been studied without preparing the mother-substance on a very large scale, and the subject did not seem to be of sufficient importance to warrant the great expenditure of time which would have been necessary for this purpose.

Action of Sodic Ethylate on Adjacent Tribromdinitrobenzol.

Seven grams of the tribromdinitrobenzol ($Br_3$1.2.3.$(NO_2)_2$4.6) were dissolved in 70 cc. of benzol and mixed with sodic ethylate in the proportion of 3 molecules of the ethylate to each molecule of the tribromdinitrobenzol. The sodic ethylate was prepared by adding the calculated amount of sodium to 70 cc. of absolute alcohol. A deep-red turbid solution was formed immediately, which was allowed to stand in a corked flask at ordinary temperatures for two days, and then filtered, the filtrate allowed to evaporate spontaneously, and the residue washed with water until the washings were colorless. The portion insoluble in water after recrystallization from alcohol showed the constant melting-point 58°, and crystallized in long, white needles, turning yellow in sunlight, but was formed in such small quantity that there was not enough for analysis; we, therefore, sought the principal product of the reaction in the portion soluble in water. The precipitate formed during the action of the sodic ethylate was dissolved in water and mixed with the wash-waters, which had previously been concentrated to a convenient bulk. The solution was then acidified with acetic acid, which threw down a black, tarry precipitate. This was filtered out, washed, sus-

pended in water, and dissolved by adding sodic hydrate to neutralization; the solution was filtered and treated with baric chloride, which produced at once a mass of shining, yellow needles. These were filtered out, washed with water, and recrystallized several times from alcohol, after which they were dried at 100° and analyzed with the following results:

I. 0.3636 gram substance gave 0.1108 gram $BaSO_4$.

II. 0.3071 gram substance gave 21.2 cc. N at 22°.5 and 765 mm. The substance was mixed with a large excess of a mixture of 8 parts of fused plumbic chromate with 1 of potassic dichromate. It was necessary to heat very gradually to avoid too rapid an evolution of the nitrogen.

	Calculated for $[C_4HBr(NO_2)_2(OC_2H_5)O]_2Ba$.	Found. I.	II.
Ba	18.33	17.91	....
N	7.47	....	7.86

The substance is, therefore, the barium salt of a bromdinitroethoxyphenol. We have not determined the constitution of this substance experimentally, but there can be little doubt that it is a derivative of resorcin, as the two bromine atoms in the meta position to each other are also in the para and ortho positions to the nitro groups, and this has been shown to be the position most favorable to replacement; whereas, the third atom of bromine, which is in the meta position to the two nitro groups, would be replaced with difficulty according to all previous work on this subject; we have no hesitation, therefore, in calling this substance the bromdinitromonoethyl ether of resorcin.

Properties of the Barium Salt.—It crystallizes from alcohol in fine yellow needles. It is nearly insoluble in water, whether hot or cold, but soluble in alcohol. It is stable at 100°, but if heated suddenly to a high temperature it explodes. Acetic acid does not decompose it.

The free bromdinitromonoethyl ether of resorcin was obtained by heating the barium salt with an acid; after recrystallization from alcohol it melted constant at 78°. It forms long, white, feathery needles, which turn yellow on standing.

The experiments just described make it highly probable

that the substance melting at 58° and insoluble in water is the bromdinitroresorcindiethyl ether. There were also other products of the reaction, as the soluble salts obtained gave a test for nitrite as well as for bromide, but they were formed in such small quantity that it did not seem to us worth while to undertake the study of them.

CXXVI.—SYMMETRICAL TRIIODBENZOL.[1]

By C. Loring Jackson and G. E. Behr.

So far as we can find, three triiodbenzols have been described in the chemical literature, but the constitution of only one has been established thoroughly ; this is the unsymmetrical (1.2.4) isomer, melting at 76° obtained by Kekulé[2] from the action of iodine and iodic acid on benzol. More recently Hantzsch[3] has also made it from the diioddiazobenzol iodide prepared from diiodaniline and found that it melts at 77°.

The other two isomeric triiodbenzols were made by Istrati and Georgescu[4] by heating together benzol, iodine and concentrated sulphuric acid. Unfortunately their original paper is not at our disposal, so that we know their work only from the abstracts of it in the "Jahresbericht über die Fortschritte der Chemie" and Beilstein's "Handbuch" (third edition). From these it appears that they ascribed the unsymmetrical constitution (1.2.4) to their compound melting at 85°, and the adjacent structure (1.2.3) to that melting at 182° to 184°, but there is no statement that they determined these constitutions experimentally. The experiments of Kekulé and Hantzsch just cited prove that the unsymmetrical isomer melts at 77° (or 76°) and, therefore, their compound melting at 85° cannot have this structure.

Under these circumstances it seemed worth while to prepare the symmetrical triiodbenzol and to determine its constitution by experiment; accordingly, we made the triiodaniline by the method of Michael and Norton,[5] that is, treating chloride of

[1] Presented to the American Academy of Arts and Sciences, December 12, 1900.

[2] Ann. Chem. (Liebig), **137**, 164 (1866).

[3] Ber. d. chem. Ges., **28**, 684 (1895).

[4] Buletinul Soc. d. Sciinte d. Bucuresci, I, 62; Jahresb. Chem., 1892, 1063; Beilstein's "Handbuch" (3d Edition), III, 73.

[5] Ber. d. chem. Ges., **11**, 111, (1878).

aniline with monochloride of iodine; and replaced the amido group in this body by hydrogen by means of the diazo reaction. The triiodbenzol thus obtained melted at 181°, which suggested that it was identical with the substance made by Istrati and Georgescu melting at 182° to 184°, and this was proved to be the case by treating it with fuming nitric acid, which converted it into a triioddinitrobenzol melting at 210°, whereas Istrati and Georgescu[1] under similar conditions obtained from their substance a dinitro derivative melting at 210° to 212°. That our triiodbenzol had the symmetrical constitution (1.3.5) was very probable, because the trichloraniline and the tribromaniline made under similar conditions are symmetrical compounds; but, as we felt it was necessary to give an absolute proof of its structure, we treated the triioddinitrobenzol with aniline, when it formed a trianilidodinitrobenzol melting at 181°. The symmetrical trianilidodinitrobenzol made by Palmer and one of us[2] from symmetrical tribromdinitrobenzol melted at 179°; in spite of the difference of 2° in these melting-points there can be no doubt of the identity of the compounds, and it follows, therefore, that the triiodbenzol melting at 181° has the constitution $I_3$1.3.5. This would leave only the structure 1.2.3 for Istrati and Georgescu's triiodbenzol melting at 85°; but in view of the fact that this compound was isolated from a mixture of the two triiodbenzols and two tetraiodbenzols, it seems to us possible that it may be the unsymmetrical isomer (1.2.4) (melting at 77°) contaminated with some of these less fusible substances. We had hoped to prepare several derivatives of the triiodbenzol, but were unable to do so in the time at our disposal, and, as we cannot continue our work together, we think it well to publish this account of the results so far obtained.

Preparation of Triiodaniline.

The triiodaniline was prepared by the method of Michael and Norton[3] slightly modified. Ten grams of aniline were dissolved in dilute hydrochloric acid, and diluted with water at 15° or a higher temperature to the volume of 7 liters. This

[1] Bul. Soc. Sci. d. Bucuresci, I, 66.
[2] This JOURNAL, 11, 455.
[3] Ber. d. chem. Ges., 11, 111 (1878).

solution was then treated with a rapid stream of air charged with the vapor of monochloride of iodine by passing it through a flask containing somewhat more than the required amount of this substance heated to about 60° by immersion in warm water. After thirty or forty minutes the action had come to an end, and the liquid was filtered as quickly as possible to remove a heavy black precipitate which had formed; the filtrate was allowed to stand for several hours, when it deposited a flocculent, buff-colored precipitate, the weight of which varied from 10 to 20 grams in different operations; that is, 20 to 40 per cent of the theoretical yield. An additional amount of the triiodaniline could undoubtedly have been obtained from the black precipitate, which was filtered out at first, but this was so impure that it seemed that more time would be lost in purifying it than in preparing fresh quantities of the second buff-colored precipitate, which, without further treatment, was pure enough for the manufacture of the triiodbenzol. That it was the triiodaniline was shown by an analysis of the substance purified by crystallization from glacial acetic acid and alcohol with the aid of bone-black, which gave 81.25 per cent of iodine instead of the 80.87 per cent required by the formula. Its melting-point was 185°. Michael and Norton give 185°.5.

The monochloride of iodine used in this work was made by the action of chlorine on iodine according to one of the methods given by Hannay,[1] and used later by Bornemann.[2] Bunsen's[3] method, which consists in boiling iodine with aqua regia, gave a less satisfactory result. Distillation of iodine with potassic chlorate, recommended by Schützenberger[4] and Hannay,[5] was not tried. Forty-two grams of powdered iodine (the amount needed for 10 grams of aniline) was treated with dry chlorine in a flask, until it had gained 12 grams; in addition to the reddish-brown liquid monochloride a considerable amount of the brilliant-yellow, crystalline trichloride of iodine was formed, which was converted into the monochloride by adding a small excess of iodine and heating the flask gently

[1] Proc. Lond. Chem. Soc., **26**, 815 (1873).
[2] Ann. Chem. (Liebig), **189**, 184 (1877).
[3] Gmelin-Kraut's "Handbuch," I, 2, p. 416.
[4] Ztschr. Chem., **6**, 1.
[5] Proc. Lond. Chem. Soc., **26**, 815 (1873).

on the steam-bath under a short air condenser until the yellow crystals had disappeared. The monochloride of iodine solidified in fine gray crystals, if cooled below 10°, and in this solid state could be kept for some time without decomposition. Its tendency to solidify made it necessary, in the preparation of triiodaniline, to use the solution of chloride of aniline at a temperature of at least 15° in order to avoid the danger of having the tube stopped up with monochloride of iodine. Although this substance melts at 24°.7 (Hannay), we found no trouble from solidification with a solution at 15°, which can be explained by the marked tendency of the monochloride to remain liquid after it has been melted.

Symmetrical Triiodbenzol,
$C_6H_3I_3$.

This substance was prepared as follows: Ten grams of the buff-colored triiodaniline, made as described in the previous section, were boiled with 125 cc. of benzol and 25 cc. of alcohol, and disregarding the undissolved portion, 5 cc. of commercial sulphuric acid were added, and then 5 grams of finely powdered sodic nitrite were sifted into the liquid as quickly as possible. As soon as the evolution of nitrogen had slackened sufficiently the liquid was boiled for some time on the steam-bath until a large part of the solvents had passed off; during this boiling a bright-yellow solid, which formed on the particles of sodic nitrite as they entered the liquid, changed its color to a light grayish-brown. After the solution had been boiled it was allowed to stand over night, and then the deposit was filtered out and washed, first with alcohol and afterwards with hot water, to remove the inorganic salts. The amount of this crude product rarely fell below 50 per cent of the theoretical yield.

The product, obtained as described above, was next sublimed from a large watch-glass heated on the sand-bath, and covered with a funnel which stood on a piece of filter-paper above the substance. If this sublimation was carried on slowly enough, as much as 80 per cent of white, glistening crystals was obtained, but if it was urged too fast the impurities also sublimed, and the crystals were yellow, or even in

extreme cases light-brown and sticky. When proper care was used, white crystals were obtained by this sublimation, even from very impure products, such as those recovered by evaporating the liquid portion of the product of the diazo reaction. The white sublimed crystals were not, however, pure, and to remove from them a persistent impurity we found repeated recrystallizations from alcohol were necessary, which finally raised the melting-point to 181°, where it remained constant. The substance was then dried at 100° and analyzed with the following results :

I. 0.1187 gram substance gave, by the method of Carius, 0.1838 gram AgI.

II. 0.1453 gram substance gave 0.2249 gram AgI.

	Calculated for $C_6H_3I_3$.	Found.	
		I.	II.
I	83.54	83.66	83.60

Properties of 1.3.5-Triiodbenzol.—This substance crystallizes from alcohol at first in radiating groups composed of a few slender prisms, which develop later into long, white prisms, frequently tapering, but always terminated by a single plane at an oblique angle to the sides of the prism. It melts at 181° and sublimes easily. It is freely soluble in benzol or carbonic disulphide even in the cold ; in chloroform it is moderately soluble in the cold, freely soluble when hot ; in ether it is moderately soluble whether hot or cold ; in glacial acetic acid or ethyl acetate it is somewhat soluble in the cold, freely soluble when hot ; in alcohol or acetone it is slightly soluble in the cold, moderately soluble when hot ; it is apparently insoluble in water, hot or cold. The best solvent for it is alcohol. Strong hydrochloric acid has no apparent action on it, even when hot ; strong nitric acid also has little or no action on it, but fuming nitric acid acts on it in the way described in the next paragraph. Strong sulphuric acid, when heated with it to its melting-point, causes a partial decomposition, taking on a dark color ; at higher temperatures the triiodbenzol sublimes out of the mixture. A strong solution of sodic hydrate seems to have no action on it, even when boiling.

An attempt was made to prepare triiodnitrobenzol ; for this

purpose 5 grams of symmetrical triiodbenzol were boiled with 140 cc. of a mixture consisting of 4 parts of fuming nitric acid with 1 part of common nitric acid. On cooling, light-yellow crystals appeared, and an additional amount of the product was obtained by pouring the acid liquid into about 1 liter of water, when a pale-yellow flocculent precipitate was formed, which was filtered out, after it had stood some time, and with the crystals weighed 5.3 grams. This was purified by crystallization from a mixture of 4 parts of alcohol with 1 of water, until it showed the constant melting-point 210°. This indicates that the substance is triioddinitrobenzol, since Istrati and Georgescu[1] obtained a triioddinitrobenzol melting at 210° to 212° from their triiodbenzol melting at 182° to 184°. For still greater certainty the substance was dried at 100° and analyzed with the following result:

0.2049 gram substance gave, by the method of Carius, 0.2644 gram AgI.

	Calculated for $C_6HI_3(NO_2)_2$.	Found.
I	69.77	69.76

The substance, therefore, is a dinitro compound, although obtained from fuming nitric acid somewhat diluted with common nitric acid. We did not have time to try whether the mononitro compound could be obtained with a still more dilute nitric acid.

The agreement between the melting-points of our triiodbenzol, 181°, and triioddinitrobenzol, 210°, with those obtained by Istrati and Georgescu,[2] 182° to 184° and 210° to 212°, establishes the identity of these substances beyond a doubt. The triioddinitrobenzol also gives us the means of proving their constitution. For this purpose 0.5 gram of the triioddinitrobenzol were heated with 0.5 gram of aniline; this proportion gives about 6 molecules of aniline to each molecule of the dinitro compound. The heating was carried on for two hours on the steam-bath, and the product, a dark-red solution, was freed from the excess of aniline by washing with dilute hydrochloric acid, when it formed a dark-red, sticky mass, which

[1] *Loc. cit.*, I, 66.
[2] *Ibid.*, I, 62, 66.

was purified by working it well with a rod under dilute hydrochloric acid and then crystallizing it from alcohol. It showed the constant melting-point 181°, which agrees sufficiently well with 179°, that given by Palmer and one of us[1] for the trianilidodinitrobenzol made from the tribromdinitrobenzol $Br_3$1.3.5.$(NO_2)_2$2.4. This proves, therefore that the triiodbenzol melting at 181° has the iodine in the position 1.3.5, as would have been inferred from its preparation from triiodaniline, which, according to the analogy of the chlorine and bromine compounds, should have the symmetrical constitution.

CXXVII.—A STUDY OF GROWING CRYSTALS BY INSTANTANEOUS PHOTOMICROGRAPHY.[2]

By Theodore William Richards and Ebenezer Henry Archibald.

Countless observers have watched the growth of crystals under the microscope. As long ago as 1839 attempts were made to study also the birth of crystals, in order to determine in what manner the new phase makes its entrance into the system. With a microscope magnifying 600 diameters, Link[3] thought he could detect the formation of minute globules at the moment of precipitation—globules which soon joined and assumed crystalline form. Schmidt,[4] Frankenheim,[5] and especially Vogelsang,[6] made similar observations some years later, and several more recent accounts of this phenomenon have appeared. Modern investigators have been more concerned with the speed of separation from supersaturated or supercooled liquids than with the form of the first separation.[7]

Ostwald, in 1891, accepted the interpretation of these data which assumes that crystallization is always preceded by the separation of an initially liquid phase, consisting of a super-

[1] This Journal, **11**, 455.

[2] Presented to the American Academy of Arts and Sciences, January 9, 1901.

[3] Pogg. Ann., **46**, 258 (1839).

[4] Ann. Chem. (Liebig), **53**, 171 (1845).

[5] Pogg. Ann., **111**, 1 (1860).

[6] Die Krystalliten (Bonn, 1875). See Lehmann, Molecularphysik, I, p. 730 (1888).

[7] Gernez: Compt. rend., **95**, 1278 (1882); Moore: Ztschr. phys. Chem., **12**, 545 (1893); Friedländer and Tammann: *Ibid.*, **24**, 152 (1897); Tammann: *Ibid.*, **25**, 441, **26**, 307, 367, **28**, 96; Küster: *Ibid.*, **25**, 480 **27**, 222; Bogajavlensky: *Ibid.*, **27**, 585.

saturated solution of the former solvent in its former solute.[1]

This explanation is indeed a plausible one, and undoubtedly holds true in cases like those studied by Schmidt and Vogelsang, where a substance separates at a temperature not far below its melting-point, and often where a substance soluble in one liquid is precipitated by the addition of a consolute liquid in which the substance is insoluble. For example, phenol always separates from aqueous solution in the form of a liquid, and manganous sulphate forms at first two liquid phases when alcohol is added to its aqueous solution. On the other hand, the separation of a high-melting salt like baric chloride from its solution in pure water is much less likely to take place in this way. In the absence of data, the behavior of such a system is rather a matter for speculation than a question to be decided by reasoning.

Ostwald has shown that an exceedingly small particle of solid is capable of starting crystallization,[2] a fact which may not be wholly foreign to the present discussion.

In any case, the matter seemed worthy of further experimenting. Ostwald says: "Die erste Bildung der Krystalle lässt sich bei Salzlösungen und dergleichen microscopisch nicht verfolgen, weil gewöhnlich im Gesichtsfeld an einer bislang gleichförmigen Stelle plötzlich ein Kryställchen erscheint." While this is true as far as the human eye is concerned, instantaneous photography, an art unknown in Link's time, seemed peculiarly fitted for the unprejudiced recording of the circumstances attending the genesis of crystals. An attempt in this direction is described below.

The problem resolved itself into the taking of a number of successive instantaneous microphotographs of a suitable mixture at the point of crystallization. This problem presented some difficulties, however. In order to secure a sufficiently brief exposure very great illumination is needed. The greater the magnifying power of the lenses of the microscope-camera, the more intense must be the source of light. The difficulty is increased by the fact that most crystals are so transparent as to absorb but little light, and reflection is possible only in

[1] "Lehrbuch", I, 1039 (1891).

[2] Ostwald: Ztschr. phys. Chem., **22**, 289 (1897).

certain directions. Hence it is hard to obtain a distinct image even in a strong light. Moreover, the machinery necessary for shifting the plates must be so frictionless in construction, and so firmly fixed, as to impart no vibration to the camera or the mobile subject of study.

These difficulties were at least partially overcome by two different arrangements, the first of which caused the successive impression of a bright image in a dark field, and the second registered dark images in a succession of bright fields. Obviously the former was the more economical as regards expenditure of sensitized film, and the simpler in execution; for when the field is dark successive images can be obtained by a very slight motion of either object or film, while, when the field is light, the whole previously exposed surface must be replaced by a fresh surface before each exposure.

The apparatus consisted of a good compound microscope fitted above with a vertical folding camera, which was supported by two massive steel pillars on the heavy stand. It was, in short, the regular photomicrographic outfit made by Bausch and Lomb. Between the microscope and camera, in a suitable light-tight box, was placed a revolving shutter, which allowed an exposure equal to one-fifth of the time of its revolution. Thus, when the shutter made two revolutions in a second, the exposure was one-tenth of a second. A Henrici hot-air motor, combined with speed-reducing double pulleys, enabled the experimenter to use any rate of revolution desired. The rate was reasonably constant, but no attempt was made to make it absolutely so. The sensitive plate or gelatin film was held above in a suitable holder, which was put in the place of the ground-glass plate used for focusing just before each series of exposures.

In carrying out the first of the two methods it was found more convenient to move the crystallizing solution than to move the photographic plate. For this purpose the slide bearing the drop of liquid was attached by a wire to a point just below the center of a segment provided above with saw teeth. The segment was moved gradually by the oscillating motion of a connecting rod, fastened by a crank to the revolving shut-

ter at one end and playing into the saw teeth on the other. In order to make the motion certain, the stroke of the connecting rod slightly exceeded the distance between the saw teeth. The segment was suspended in such a way that its center of gravity coincided with its point of support, and the friction of its bearings was so adjusted that it would move easily, and yet remain stationary during the return stroke. The distance through which the observed object was moved was easily varied by altering the relative lengths of the lever-arms; distances varying from one-tenth to one-fiftieth mm. were generally used. The shutter was so arranged that during the exposure the segment and slide were at rest, the shift in position being effected during the four-fifths of the revolution through which the shutter was closed. The accompanying diagram will make the arrangement clearer.

The diagram represents the apparatus an instant before an exposure begins.

As a source of light any ordinary combination of incandescent electric lights proved to be inadequate. A good Auer von Welsbach light with a powerful reflector was more satisfactory, but the best results were obtained with the help of sunlight directed by a suitably arranged mirror and condensed by reflectors and lenses. The chief, though not serious, difficulty of this arrangement was the great heat caused by the converging rays, a difficulty which was obviated partially by an absorbent screen in some later experiments.[1]

The first photographs were taken by reflected light, the drop of solution being placed upon a ruby-colored slide. As soon as the crystallization had begun upon one edge of this drop the very sensitive plate was uncovered and the shutter and segment were set in motion. The exposure was stopped after 15 or 20 revolutions, so as to avoid confusing superpositions. Even with the strongest light the images were very faint and unsatisfactory; it is not worth the space to reproduce them here.

Another mode of obtaining light images on a dark ground, applicable to all except the isometric system of crystals, is the

[1] Hutchins has shown that pure water is as good as a solution of alum for this purpose (Am. J. Sci., 143, 526 (1892)).

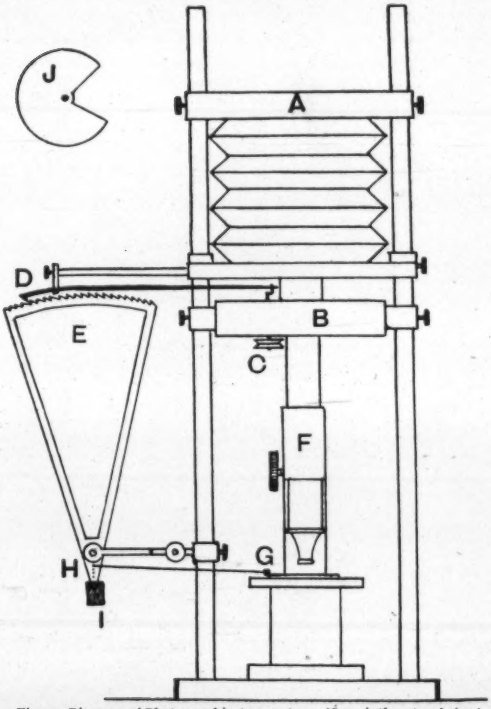


Fig. 1. Diagram of Photographic Apparatus. (One-sixth natural size.)

A, sensitive plate or film holder.
B, box containing shutter.
C, pulley attached to axle of shutter to communicate power from motor.
D, light rod moved by crank attached to same axle; D is guided by a stout support in which it moves loosely.
E, segment provided with rachet teeth; moved gradually by rod D.
F, microscope.
G, slide for object, moved by wire running to H.
H, holes to regulate amplitude of object's motion.
I, weight, balancing segment.
J, horizontal projection of revolving shutter in detail.

use of polarized light.[1] A Nicol prism was placed in the barrel of the microscope and another just below the stage. The main body of the light was thus intercepted by the crossed prisms, and only that which had been deflected by the crystalline structure was allowed to emerge. It is true that this method could not, in all probability, decide the chief point at issue; for the prenatal globular condition of crystals would probably have no effect on polarized light. Definite optical structure is of course necessary to produce the required deflection of the plane of polarization, and such definite structure might not be possessed by the globules. Nevertheless, the idea seemed well worth a trial.

The images were now much more clearly defined and striking, and with a magnification of 30 diameters, 10 sharp impressions, each exposed one-fiftieth second, could be obtained in a second. For this low power the eyepiece was removed from the microscope and an objective with long focal distance alone was used to give the image. The degree of enlargement was obtained by actually measuring the image of a micrometer scale divided into 0.1 mm. The rapidity of exposure was so great that many plates were sacrificed, for it was difficult to find the precise moment when nascent crystals were in the field of view. In most cases the crystallization was already well started when the exposure began, as in Fig. 4; but in some nothing but blank negatives were obtained. The best method is so to arrange circumstances as to have the crystallization begin upon one edge and spread slowly over the drop. Another difficulty was the attaining of the exact actinic focus, which differed slightly from the visual focus. It was found that a definite fraction of a revolution in the fine adjustment of the instrument or a definite shift of the sensitive plate could be relied upon to cover this difference, when experiment had once found the right spot.[2]

Among other substances sodic nitrate, baric chloride, cupric sulphate, and ferrous ammonic sulphate were found to give

[1] This suggestion was kindly made by Prof. E. C. Pickering.

[2] Of course an apochromatic lens would have saved us this trouble, but our device answered sufficiently well and was less expensive. Such lack of definition as may be observed in the plates was due rather to the behavior of the object than to optical imperfection.

Plate I.

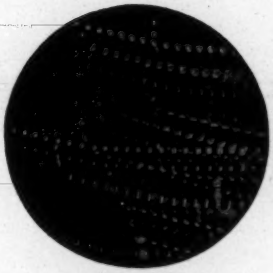


Fig. 2. Baric chloride; 30 diam.; exposure 0.04 sec.

Fig. 3. Baric chloride; 30 diam.; exposure 0.08 sec.

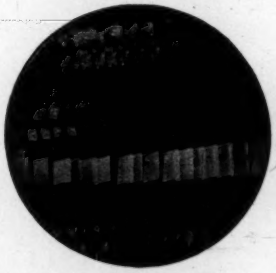


Fig. 4. Sodic nitrate; 30 diam.; exposure 0.10 sec.

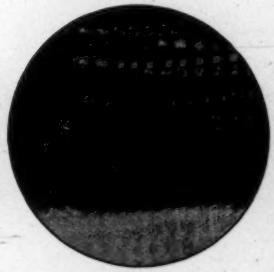


Fig. 5. Sodic nitrate; 30 diam.; exposure 0.12 sec.

Fig. 6. Baric chloride; 110 diam.; exposure 0.10 sec.

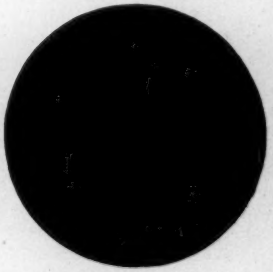


Fig. 7. Cupric sulphate; 110 diam.; exposure 0.12 sec.

satisfactory results. A few photographs chosen as being typical examples of many negatives are given here. (Plate I. Figs. 2, 3, 4, 5.)

All the images recorded on these plates are perfectly sharp and regular when in focus; but the magnifying power was too low to give important evidence concerning the birth of the crystals. The crystals always first appear as points, indicating a diameter of less than $\frac{1}{100}$ mm. The regularity of growth of those already well started is worth a passing mention.

The next objective used gave a magnification of 110 diameters. With this power the light was so much diminished that exposures of less than one-fifteenth second became too pale. Three examples from among these negatives are given below. It will be noticed that in all cases the crystals have their regular forms when they first appear upon the plate. Another point worthy of attention is the fact that the growth in diameter at first is more rapid than it seems to be subsequently. This rapid growth of small particles has already been noticed by Ostwald;[1] it is treated more fully in the following pages. The crystals of sodic nitrate grew faster than those of baric chloride or cupric sulphate, and the two latter substances evidently appeared at first in very thin plates. It is interesting to note that the thickening of these plates caused a corresponding change in the quality of the emerging light, and hence the crystal images show a rhythm of dark and light. (Plate I., Figs. 6 and 7; Plate II., Fig. 9.)

At this point the whole method of procedure was changed on account of the probability that a globular condition, if it existed at all, would not be visible through the crossed Nicols. The apparatus was now arranged for the exposure of successive portions of a film to unpolarized sunlight emanating from a bright field, upon which the crystals appeared as dark spots. The slide and crystallizing solution were allowed to remain stationary, and the gelatin film was moved, as it is in the common film-cameras. The 2.5-inch Eastman cartridge film was found to answer the purpose. At first the turning was effected by an automatic electromagnetic arrangement which

[1] Ztschr. phys. Chem., **22**, 320.

received its current from a make-and-break contact attached to the shutter. Since a current of 10 amperes was needed to secure a sufficiently forcible and speedy action, the operation of this device was somewhat troublesome, and when the exposures were not much more frequent than one a second the film was rolled by hand. A suitable signal attached to the shutter axle, which was still turned by the Henrici motor, gave the necessary indication of the proper moment for renewing the sensitive surface. With this apparatus it was of course possible to obtain photographs of isometric crystals, which could not be examined with the preceding arrangement.

At first a power of 100 diameters was employed, and very satisfactory pictures of the growth of crystals of potassic iodide were obtained. One of these negatives is reproduced here as an example. (Plate II., Fig. 9.) They showed nothing new, however; hence a much higher power of 580 diameters was applied by combining a "2-inch" eyepiece with an "$\frac{1}{8}$-inch" objective. With this contrivance the light was, of course, far less intense, and the definition less sharp. Even with the brightest sunlight, concentrated by mirrors and an Abbe condenser, the exposure could not profitably be made less than one-eighth second. These plates have been enlarged by usual processes to over seven times their original size, so that a total enlargement of over 4,000 diameters has been attained. Since these larger images were not much more clear than the smaller ones, while they occupy much more space, the plates herewith given are all from the original negatives.

A number of good impressions of crystallizing potassic iodide were taken under these circumstances, but many other rolls were sacrificed. The chief difficulty, as before, was to secure the right moment, and this difficulty was, of course, much augmented by the limited expanse of the field. Prints from a few of the successful negatives are given below. In order to give a clear impression in printer's ink, these were much intensified by successive photographic printing and intensification; but, of course, no attempt was made to remove the imperfections of the successive plates, for which allowance may easily be made. (Plate III., Figs. 10 to 15.)

Plate II.

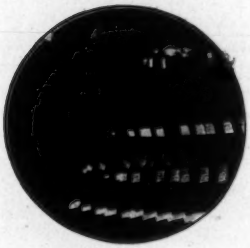


Fig 8. Sodic nitrate; 110 diam.; exposure 0.12 sec.

Fig. 9. Potassic iodide: 100 diam.; exposure 0.25 sec.

The study of these photographs reveals several interesting points. In the first place, it is noticeable that no image is wholly without evidence of crystalline structure. The most doubtful cases are those in Figs. 9 and 11; but the elongated shape of these doubtful images seems to indicate a solid. A globule of a new liquid phase, $\frac{1}{1000}$ mm. in diameter, would have left an unmistakably circular image on the highly magnified plate, for its index of refraction could not have been identical with that of the aqueous solution. The fact that we could not find such a globule, of course, does not prove that a globule cannot exist, either for an infinitesimally brief period of time, or of an infinitesimal magnitude beyond the reach of microscopic observation. Nevertheless, so many scores of photographs were taken as to diminish considerably the probability that such globules can ever be seen with substances possessing a high melting-point.

A striking fact to be noticed in nearly all the most highly magnified records is the ill-defined appearance of the smallest crystals. This appears to be due, not to a lack of structure, but rather to the rapid growth in diameter, which is manifest in the young crystal. The initial rapidity is so great that the fifth of a second appears to include several different stages of growth, and hence a blurred impression results. It is easy to obtain some idea of the rapidity of this initial growth by comparing the sizes of the first two or three appearances of each crystal.

With this object a few of the series were measured by means of an accurate micrometer; but the conditions of the experiments are too uncertain to give the very precise measurements much value. Perfect constancy of temperature and evaporation, as well as in the rate of the revolving shutter, involving grave complications in the apparatus, should of course be maintained if great accuracy is attempted. Measurements with a fine millimeter scale afford all the precision which it is worth while to attain under present conditions. A typical case (Fig. 9, largest crystal) gave the following measurements in millimeters for the successive longest diameters: 2.0, 2.6, 3.0, 3.2, 3.3, 3.5, 3.7, 3.9, 4.1, 4.2, 4.4. The actual sizes of the crystals were, of course, only a hundredth of these

measurements, since the enlargement was 100 diameters.

In spite of the inexact nature of such measurements, it is possible to use them as a means of defining approximately the law regulating the changes in speed. The following table details six series of corresponding diametric measurements of six crystals taken at random. The measurements were taken directly from the photographs in millimeters.

Diameters of Successive Images.

	Crystal 1.	Crystal 2.	Crystal 3.	Crystal 4.	Crystal 5.	Crystal 6.
First appearance	1.0	2.0	3.0	3.0	4.0	2.5
Second "	1.6	2.6	5.7	6.0	6.7	3.5
Third "	1.7	3.0	6.8	7.0	7.8	4.1

These all show greater growth in the first interval than in the second. In order to reduce them to one standard, the diameter of the third appearance was taken in each case as unity. The table then becomes :

Diameters of Successive Images.

	Crystal 1.	Crystal 2.	Crystal 3.	Crystal 4.	Crystal 5.	Crystal 6.	Average.
First appearance	0.59	0.67	0.44	0.43	0.51	0.61	0.54
Second "	0.94	0.87	0.84	0.86	0.86	0.85	0.87
Third "	1.00	1.00	1.00	1.00	1.00	1.00	1.00

At the time of the first appearance the average age of the crystal must be about half the time intervening between two exposures ; for the crystal must have been formed since the last exposure, and it is as likely to come near the beginning as near the end of the interval. Thus, in Fig. 11 the crystals evidently started immediately after the previous exposure, while in Fig. 9 they were registered while still very young. The averaging of a much larger number of observed diameters led to the slightly different values given below, corresponding to the accompanying times :

Time = t.	Diameter = D.
0 interval	Diameter 0
0.50 "	" 0.57
1.50 intervals	" 0.87
2.50 "	" 1.00

These data are plotted in Fig. 16.

Plate III.

Fig. 10. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

Fig. 11. Potassic iodide ; 580 diam. ; exposure 0.25 sec.

Fig. 12. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

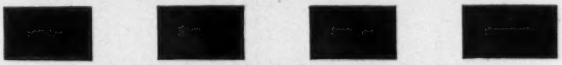


Fig 13. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

Fig 14. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

Fig. 15. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

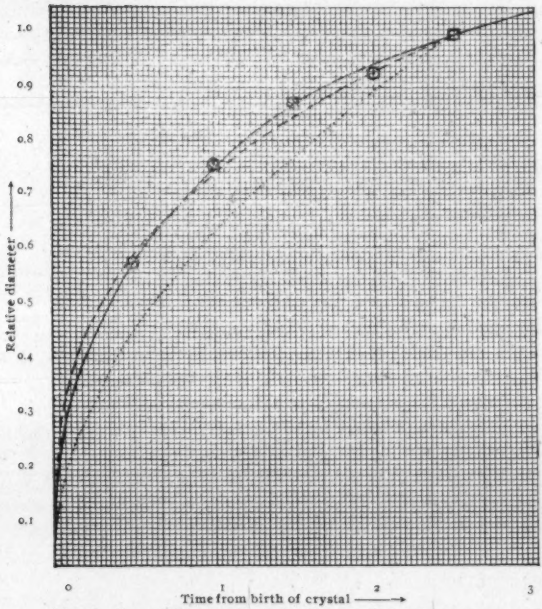


Fig. 16. Diagram Representing Rate of Increase in Crystal Diameter.

□ represents point from average of crystals taken at random.
O represents point from average of selected crystals.
——— represents probable actual rate of growth.
– – – represents equation $D^2 = kt$.
····· represents equation $D^3 = kt$.
The unit of time is the time of one revolution of the shutter, or 1.25 seconds.
The substance was potassic iodide.

The inspection of the figure shows at once that the curve is similar in general shape to one represented by the equation $D^n = kt$, where D is the diameter of the crystal, t the time from the birth of the crystal, and k a constant. The only question is as to the magnitude of n. The curves which result from the assumptions $n = 2$ and $n = 3$ are given above, for comparison with the experimental curve. It is clear that the curve with the latter value, $n = 3$, is the nearest, possess-

ing the same general curvature, and deviating from the average less than the individual measurements do. This is equivalent to saying that *equal increments of time correspond to equal increments of volume*, instead of equal increments of *surface*, as one might have supposed. Of course a law based upon such merely approximate data cannot be considered as definitely settled; but clearly the general character or tendency of the curve is established. It is probable that under the necessarily ill-defined conditions of our experiments the growth follows no one law with precision; supersaturation, convection, diffusion, and evaporation must all influence the result. The crystal which seems to have deviated most widely from the average is that depicted in Fig. 10; this crystal grew at first less rapidly than usual, and finally came almost to a standstill. It is possible that an increasing solubility due to increasing temperature may have caused this delaying tendency.

It is interesting to compare this average, calculated on the assumption that the crystal starts in the middle of the dark interval, with a few single cases which appear to have begun to crystallize very near the beginning or end of the interval. In these cases, the first image of the crystal will appear either almost as large as the second image, or very small compared with it. It will appear almost as large as the second image when the preceding exposure has just not caught the beginning of the crystal, which has thus had a whole interval for growth; or very much smaller than the second image when the first impression has registered a crystal only a very small fraction of a second old. Marked examples of the former case are to be found in Fig. 11, and of the latter in the largest crystal in Fig. 9, and the smallest crystal in Fig. 15. The times of revolution represented by Figs. 9 and 11 are the same, 1.25 seconds, and the other conditions also were identical, hence we may compare these with accuracy. Careful measurements of the sizes in Fig. 9 showed the first large impression of the crystals to be about 80 per cent of the diameter of the next impression, and approximately the same relationship appears in Fig. 11. In order to find if this relationship corresponds with the equation $D^3 = kt$, the larger diameter is assumed to be 0.93, the theoretical value corre-

sponding to two intervals of time, if that corresponding to two and one-half intervals is taken as unity. Hence the smaller one becomes 0.75, corresponding to one interval of time, a value, marked in a circle on the diagram, which is surprisingly near the cubic curve. Hence the equation $D^3 = kt$ is confirmed. That the same curve holds approximately for the further growth of the crystal is manifest by a quantitative study of Fig. 9 (Plate II.).

In this connection it is interesting to note that the crystal seems often to grow at first in the same proportion in all directions. Even the very minute image in the center of the second exposure, given in Fig. 9, shows itself under the microscope to be elongated like the crystal which grows from it. In the next exposure this crystal had the proportions 0.02 mm. × 0.0125 mm., and after four more exposures it still had almost exactly the same proportions, being 0.035 mm. × 0.022 mm. After two or three more seconds the form given in Fig. 9 began to change slightly, the crystal becoming slightly less elongated in shape; but by this time the neighboring crystals had grown so much as to approach it, and hence to alter the conditions. A similar constancy in proportion may be observed in many other series here given.

The diagram shows how exceedingly fast the diametric growth of the crystal must be in the first tenth of a second of its existence. Hence we have an explanation for the suddenness of its appearance to the eye of an observer, and for the blurred edges of its photographic image. It is true that another cause may contribute to the blurred effect; namely, the irregular refraction caused by the convection of the lighter solution which has just deposited part of its load; but the speedy growth alone is capable of explaining the observed indistinctness.

Interesting as the rapid initial growth in diameter may be, it places a serious bar in the way of more precise study of the birth of crystals. One clearly needs not only high magnifying power but also great speed; and these two together require very intense light. Whether or not we shall be able to obtain more positive knowledge with the present apparatus is questionable. The same phenomenon casts a meas-

ure of doubt over some of the observations of Link and his followers. Is it not possible that the subjective effect of the rapidly growing crystal might be mistaken for that of a globule of liquid? Even upon the photographic plate there is a slight resemblance, and in one or two cases deliberate study is needed to detect evidence of structure in the smallest crystals.

In conclusion, the report of the foregoing pages may be summarized as follows: It has been found possible to take very frequent photomicrographs of crystals during their birth and growth. An enlargement of over 4,000 diameters was obtained, and both common and polarized light were used. Only substances with high melting-points were examined, and the crystallization was always from aqueous solution. No properly focused image on any of the plates seemed to be devoid of crystalline structure. The growth in diameter during the first second of the crystal's life was found to be vastly greater than during the subsequent period. Not the diameter itself, but a power of the diameter, was proportional to the time under the conditions used in our experiments. This exceedingly rapid initial diametric growth accounts for a lack of definition noticed in the first images,—a lack of definition sufficient to have misled the eye, but not enough wholly to obscure the photographic evidence of crystalline structure.

Hence we may conclude that whatever theoretical reason there may be for believing that crystals always develop from a transitory liquid phase, the present experimental evidence is inadequate to prove that these globules attain a size visible in the microscope, except in the case of substances which melt at temperatures not far from the temperature of crystallization. The present paper is to be regarded rather as the suggestion of a mode of study than as a finished treatment of the subject, however.

The apparatus might be used to obtain a series of kinetoscopic pictures of insects or other small animals or plants, and is now being used for the study of the change in structure of steel at high temperatures. We are indebted to the Rumford Fund of the American Academy of Arts and Sciences for much of the apparatus used in this work.

CAMBRIDGE, MASS., October, 1898,
to October, 1900.

CXXVIII.—THE SOLUBILITY OF MANGANOUS SULPHATE.[1]

By Theodore William Richards and Frank Roy Fraprie.

The solubility of manganous sulphate has been carefully determined within the past year by F. G. Cottrell,[2] and the present paper is written to confirm in some measure the results of his work. He was able to disprove, by well-considered experiment, the less recent work of Linebarger,[3] who published a singular series of results resting upon faulty reasoning and an erroneous method of experimentation. In a case of this kind, when authorities differ, the truth is more quickly acknowledged when it is supported, hence the publication of the present paper.

The work to be recorded below was done in the spring of 1898, long before the work of Cottrell. It was part of a still unfinished investigation which has as its object the study of the transition equilibria of potassic manganous sulphate. We hope that circumstances may permit the early publication of the remainder of this work, which has been suspended for a time.[4]

It was soon found that a much higher temperature was necessary to drive off the water of crystallization of manganous sulphate than has usually been supposed. Linebarger used only 180°, at which temperature at least 1 molecule of water remains in the salt if it is surrounded by air with the usual proportion of aqueous vapor. The handbooks name 210° to 240° as the temperature required, and Cottrell, calling attention to Linebarger's error, used 280°. We found that traces of water still remained after heating for half an hour at 350° in an air-bath. In this respect the substance reminds one of cupric sulphate.[5] The amount thus retained does not much exceed the tenth of a per cent, and the effect upon Cottrell's results could not have been serious. On the other hand, a temperature just below redness, perhaps 450°, obtained with a

[1] Presented to the American Academy of Arts and Sciences, March 13, 1901.

[2] J. Phys. Chem., **4**, 637 (1900).

[3] This Journal, **18**, 225 (1893).

[4] A brief statement of the scope and object of this work will be found in Proc. Am. Assoc. Adv. Sci., 213 (1898).

[5] Richards: Proc. Am. Acad., **26**, 240 (1891).

carefully watched naked flame, and applied after drying at lower temperature, was capable of driving off in five minutes so much of the water that subsequent similar heating for a quarter of an hour showed only an average loss of 0.2 mg. The product was wholly soluble in water, showing that no decomposition of the sulphate itself had occurred.

The manganous sulphate was purified with great care, and the crystals employed were coarsely powdered. The specimen whose solubility was to be determined was put into a large, stout test-tube with a carefully cleaned rubber stopper, and was kept for at least four hours at the desired temperature in an Ostwald thermostat before a sample was taken. The agitation of the mixture was active and continual, being effected by an apparatus similar in principle to that of Schröder.[1] The motive power was a Henrici hot-air motor. At the close of the appointed time the sample to be analyzed was removed by an effectual filtering pipette, somewhat similar to one which has since been used in van 't Hoff's laboratory.[2] A diagram of the pipette is appended. The cotton was necessary to filter off the fine powder which appeared during the stirring. In order to avoid change of temperature, the pipette was previously warmed by placing it in a dry test-tube immersed in the thermostat. Only the mouth of the test-tube was allowed to project above the water of the thermostat, and of course every precaution was taken to obtain a fair sample of the solution.

Filtering pipette.
The filtering attachment, filled with cotton wool ("absorbent cotton" C), is temporarily attached to the jet A of a 5-cc. pipette by means of the rubber tube B.

After filling the pipette and quickly removing the rubber filtering-jet attached to

[1] Schröder: Ztschr. phys. Chem., 11, 454 (1893); Noyes: *Ibid.*, 9, 606 (1892). For details see Richards and Faber: This JOURNAL, 21, 168 (1899).

[2] Van 't Hoff and Meyerhoffer: Ztschr. phys. Chem., 27, 79 (1898).

it, the clear solution was run into a weighing-bottle and was quickly stoppered and weighed. The known amount of solution was washed into a roomy platinum crucible, when it was cautiously evaporated, and the residue was ignited in the fashion already described. In order to make certain that no transition had occurred during the experiment, the crystal water contained in the solid phase left over after the saturation was always determined. Below are the data thus obtained:

The Solubility of $MnSO_4.5H_2O$ at 25°.

No. of determination.	Time of saturation. Hours.	Weight of solution. Grams.	Weight of $MnSO_4$. Grams.	$MnSO_4$ for 100 grams water. Grams.
1	6	5.0342	1.9849	65.09
2	6	6.3405	2.4947	64.89
3	8	4.4318	1.7470	65.07
4	8	5.2465	2.0656	64.94
Average,				64.99
5	48	3.4514	1.3622	65.20
6	72	3.5349	1.3947	65.17
Average,				65.19

Cottrell found 64.78 as a mean of two closely agreeing determinations, but the time allowed for saturation was only two and one-fifth hours. The probable reason for his slightly lower result will be discussed below.

The solubility of the tetrahydrate is recorded below:

The Solubility of $MnSO_4.4H_2O$ at 30°.15 and 35°.0.

No. of determination.	Temperature.	Time of saturation. Hours.	Weight of solution. Grams.	Weight of $MnSO_4$. Grams.	$MnSO_4$ for 100 grams water.
7	30°.15	4	4.3125	1.7215	66.44
8	30°.15	4	5.7567	2.2943	66.27
9	30°.15	4	4.5992	1.8339	66.32
10	30°.15	4	5.2322	2.0894	66.48
Average,					66.38
11	35°.0	13	3.7009	1.5007	68.21
12	35°.0	14.5	2.7854	1.1296	68.22
Average,					68.22

The solid material taken from the tubes in Determinations 7 to 10 contained as much as 4.3 molecules of water for each $MnSO_4$, but it was, nevertheless, probably the designated hydrate containing included mother-liquor. The greater solubility of the pentahydrate at 30° would certainly involve the solution of any accessible pentahydrate. The salt remaining from Determinations 11 and 12 contained 4.03 molecules of water.

The results at 30°.15, giving an average of 66.38, correspond almost exactly with Cottrell's figure, 66.43 at 30°; but in this case his time of saturation was increased to an average of three hours, while ours was not much longer. Hence close correspondence was to have been expected, and the figures mutually support one another. The slight difference may be due to a residual trace of water in Cottrell's salt.

On the other hand, at 35° Cottrell used only two hours for saturation, while we used about seven times as much time. Hence the difference between his result, 67.87, and ours, 68.22, may be explained once more by a difference in the time of mixing.

Until recently the cause of this difference would have been ascribed to a possible incomplete saturation in Cottrell's case; and the higher figures, other things being equal, would have been accepted as the more accurate.

While this may be true, the recent work of Ostwald[1] on the solubility of powders and the surface-tension of solids has thrown new light on this matter, and it seems quite possible that neither series of results may be perfectly definite. Fine powders have a greater solution-tension than coarse ones, for the same reason that small drops have a greater vapor-tension than large ones.

It has often been stated that very long agitation is necessary to secure saturation.[1] In view of Ostwald's newer work it seems quite possible that continued active agitation introduces an uncertainty even greater than the one which it

[1] Ztschr. phys. Chem., 34, 495 (1900).

[2] For example, see "Ostwald's Physicochem. Measurements," Walker (Macmillan, 1894), p. 176.

avoids. The crystals of salt in the ever-moving tube act as mutual millstones, and gradually wear off one another's corners, with the production of fine powder. This fine powder must continually dissolve, because it is more soluble than the larger aggregations. At first it will simply hasten the speed of attaining saturation; but later, when saturation with respect to the larger particles has been attained, the fine powder will tend to produce a solution supersaturated with respect to those larger particles. The experience of Cottrell and others seems to indicate that supersaturation is harder to obviate than inadequate saturation. Cottrell, for example, found that $MnSO_4.H_2O$ attained a concentration of 57.41 grams in 100 grams of water after two hours of agitation when the salt was added to pure water, while after twice as long a time the supersaturation in another tube had only been reduced from 72.5 to 62.3 grams per 100. The solubility found after twenty-seven hours, when both methods gave the same result, was 58.32, or 0.91 gram more than the first and 4 grams less than the second figure.

The outcome of the matter seems to be that constant results upon solubility are usually obtained only when the rate of production of the fine powder exactly balances the rate at which the supersaturation is relieved, and that constant results thus reached represent only a compromise. With cautious agitation, it is possible that a solubility very near that of flat crystal surfaces might be obtained; on the other hand, very active agitation, such as we used, must tend to increase this solubility almost to that corresponding to the fine powder which we always observed in our tubes.

Every one will agree with Ostwald in deciding that the solution-tension of flat surfaces, rather than that of sharply curved surfaces, is the quantity which should be determined, if possible. This result would be best obtained by keeping the solid as free as possible from agitation, and driving a constant current of the saturating solution over these resting crystals. A dissolving apparatus which has recently been described, if assisted by a small turbine and suitably immersed in a thermo-

stat, would perhaps be the safest apparatus, although complete saturation would require much time.[1]

It is evident, as Ostwald points out, that most published determinations of solubility, those of Cottrell and our own included, are subject to a small uncertainty; but it is also evident that the work of Cottrell is by far the most complete work upon the solubility of manganous sulphate which has been published, and that it wholly overthrows the erroneous results of Linebarger.

We determined also the solubility of both the dihydrate and the tetrahydrate of the double sulphate of manganese and potassium, and found solutions saturated at 25° with both or either hydrate to yield 40.1 grams of anhydrous solid. Hence this temperature must be near the transition temperature of the two hydrates. The detailed publication of these results and many other similar observations must be reserved for a later communication.

In a few words of recapitulation, the present paper may be said to confirm the work of Cottrell and to disprove that of Linebarger, while a measure of doubt is cast upon the usual methods of determining solubility.

CAMBRIDGE, MASS., February, 1901.

THE PREPARATION OF OSMOTIC MEMBRANES BY ELECTROLYSIS.

BY H. N. MORSE AND D. W. HORN.

The difficulties with which Pfeffer had to contend in the preparation of suitable semipermeable membranes for the investigation of osmotic pressure are well known and need not, therefore, be rehearsed. Yet, notwithstanding the importance of the subject, no suggestion appears to have been made up to the present time which has helped to obviate any of those difficulties or in any degree to lessen them. The method of Pfeffer has not been improved, and, judging from the testimony of many who have tried it, attempts to prepare the Pfeffer cell usually fail to give satisfactory results.

[1] Richards: This JOURNAL, 20, 189 (1898).

In this connection, it occurred to the authors that if a solution of a copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions must meet in the interior of the wall and separate as copper ferrocyanide at all points of meeting, so that in the end there should be built up a continuous membrane well supported on either side by the material of the wall. The results of our experiments in this direction appear to have justified the expectation and to be worthy of a brief preliminary notice.

The first problem concerned, of course, the effective removal of the air in the walls of the porous cups, since the presence of air obviously interferes with the formation of a sound membrane. For this purpose we have taken advantage of the strong "endosmose" which appears when a current is passed through a porous wall separating two portions of a dilute solution in which the electrodes are immersed. A boiled solution of potassium sulphate containing about 0.5 gram of the salt in the liter was filled into the porous cup and into the beaker in which it was placed until the level of the liquid within and without reached nearly to the edge of the cup. On passing the current between the electrodes in the direction of the one within the cup, the liquid in the cup rises with a rapidity which increases with the dilution of the solution and with the intensity of the current. The water, in passing through the wall, appears to sweep out the air in an effective manner. As the liquid within the cup rose, it was removed from time to time with a pipette or by means of an intermittent siphon and replaced by pouring more of the solution into the liquid outside the cup. The quantity of water forced through the wall in this way was considerable. As a rule, we have continued the electrolysis of the sulphate until 300 cc. had been removed by the pipette or siphon, which required ordinarily about one hour. The cup was then emptied, washed, and placed in a large volume of distilled water until required for the deposition of the membrane.

To form the membrane, the wet cup was placed in a beaker

and surrounded with an electrode of sheet copper, which completely encircled it. The other electrode—the one within the cup—was of platinum. After fixing the electrodes and connecting with the dynamo so that the current should begin to flow the instant the liquids touched the opposite walls of the cup, the copper solution (N/10 or N/5 sulphate) and that of the potassium ferrocyanide (also N/10 or N/5) were introduced as nearly simultaneously as possible. At first there is considerable endosmose in the direction of the current, *i. e.*, from the copper solution into that of the ferrocyanide, but no copper has ever been found to enter the cup, neither have any of the ferrocyanogen ions made their way into the copper solution. Both walls remained perfectly clean and free from discolorations except in a few instances, in which, for some reason not yet determined, metallic copper was deposited on the outside of the cup. At the upper edge of the cup, however, nearly midway between the two sides, there soon appears a line of reddish-brown color, showing in general the position of the membrane with respect to the outer and inner walls of the cup. The resistance usually rises quite rapidly, reaching in extreme cases 3,000 ohms within an hour, while the endosmose diminishes correspondingly. The most rapid rise in resistance is observed in the less porous hard-burned cups. In the softer and more porous ones, the resistance may not exceed 200 or 300 ohms within an hour; and after a time, in such cases, the resistance begins to fall, owing apparently to the action of the accumulated alkali upon the membrane. If the solution of ferrocyanide in the cell is then replaced by a fresh one, the resistance begins to rise again.

Having obtained the desired resistance, the cell was removed, rinsed inside and out, filled with distilled water, and placed in a beaker containing water, care being taken, of course, not to allow any of the liquid from the inside to come in contact with the outer surface of the cup, and *vice versa*.

Our first experiments were with ordinary porous battery cups holding approximately 250 cc. On treating some of these in the manner described above until a resistance of from 1,500 to 3,000 ohms had been reached, they were tested as to the

presence of a sound membrane within their walls by filling them one-third full of a normal solution of sugar and then immersing them in water until the liquids within and without were on the same level. The water entered quite rapidly and the cups usually began to overflow within from fifty to seventy-five hours. On breaking the cups, the membrane could be seen as a thin line along the fracture surfaces. Ordinarily it was located about midway between the two walls except where the material of the cup manifestly lacked uniformity. In such places the line would bend to one side or the other, and again return to its original direction beyond the uneven spots. The experiment was repeated with the same result with samples of all the various kinds of porous battery cups which had accumulated in the laboratory. It was found that a membrane which would at least exhibit osmotic activity could be made in the walls of any of them without difficulty. It was also tried with certain other cups which had been specially made with a view to the rapid filtration of liquids and which were, therefore, much more porous than the ordinary battery cup. We could form a membrane in these, but it was necessary to exercise some care in the control of the current. Otherwise the resistance would occasionally drop in a marked degree, indicating a rupture of the membrane. The resistance, in the case of the cups last mentioned, could not be raised above a certain point, which was far below that which could easily be obtained in less porous cups.

With a view to testing the power of the electrolytically prepared membrane to resist pressure, we had made at a local pottery some bottle-shaped cells having a capacity of about 250 cc. After depositing the membrane in these, in the manner described, they were filled with a normal solution of sugar, closed with rubber stoppers through which glass tubes had been passed, and placed in beakers of water standing upon the floor. Other lengths of tubing were added until the ceiling, 5.5 meters above the floor, was reached. Our tubes began to overflow in periods ranging from six to fifteen hours. When the open manometers were replaced by closed ones containing mercury, the cells failed; not, however, in consequence of

ruptured membranes. In manufacturing such vessels, the bottom is made separately and is inserted and cemented in its place after withdrawing the mold upon which the rest of the bottle is formed. The union between the two parts proved to be a weak one in the case of our cells. Before any considerable pressures were reached the bottoms gave way, permitting the sugar solutions to escape. In most instances the line of detachment could be seen, but not in all. We therefore added a little ferrocyanide to the solutions of sugar and a little copper sulphate to the water in which the bottles stood in order to ascertain whether any of the sugar escaped at other places. A reddish-brown circular line then appeared where the two parts had been joined, but nowhere else.

Our next experiments were with small porous cups, such as are employed in making standard battery cells. These were about 85 by 25 mm., internal measurement, and were provided with a flange at the top. We had found by previous experience that the forcing of a stopper into a cell is liable to injure the membrane, hence we cemented glass tubes in the cups before forming the membranes. In order to make the union more secure, channels were cut on the inside of the cups a little below the rim and parallel to it. The glass tubes, 125 mm. long and with external diameters somewhat less than the internal diameters of the cups, were provided with rubber rings at one end, of such thickness that rubber and glass together made moderately tight stoppers for the cups. These were pushed into the cups until the upper edges of the rubber rings were a little below the channels. The spaces above the rubber were then filled with the cement, which was made by mixing 5 parts of litharge with 1 part of glycerine. After hardening for forty-eight hours, the exposed surface of the cement was painted, to protect it from liquids, with a solution of equal parts of rubber and paraffin in carbon bisulphide. The cups were then freed from air and the membranes deposited in the usual manner. When the rubber stoppers carrying the closed manometers were inserted, provision was made for the escape of the superfluous sugar solution by manipulating a small steel rod between the rubber and the glass. The rod

was afterwards extracted with a pair of forceps. In the first cell prepared in this way the pressure rose within an hour to 3.25 atmospheres, when the stopper began to give way. It was again crowded into place, and the pressure rose to a little over 3.5 atmospheres, but from this point the stopper was slowly pushed out of the tube. We then emptied the cell and shrunk the end of the glass tube in the flame to about three-fourths its original diameter, in order to give the stopper a more secure hold in the glass. With this modification we were able to secure pressures a little above 4.5 atmospheres. At that pressure, however, the sugar solution always began to ooze out between the manometer and the rubber stopper, and the stopper itself to move upward out of the tube.

We have found it impossible, with the crude manometer hitherto employed by us, to test our membranes at pressures much above 4.5 atmospheres; and it is clear that, to do this, rubber stoppers must be dispensed with and some suitable metallic connection devised to join the manometer to the cell.

We have made no attempt as yet to measure osmotic pressure, our object at present being only to test the strength of the membranes. It seems improbable that the total osmotic pressure of concentrated solutions, *e. g.*, molecular-normal ones, will ever be directly measured. It should, however, be practicable to construct cells in which the pressure of dilute solutions can be quite accurately determined. In that case, it should be feasible to measure the pressures of more concentrated ones by a differential method. For example, having obtained a membrane of such quality in a cell of such construction that the osmotic pressure of a tenth-normal solution can be satisfactorily measured, the pressure of a two-tenths normal solution could be determined by immersing the cell, not in water, but in a one-tenth normal solution, etc. It is probably safe to predict that if a method of determining molecular weights or electrolytic dissociation, by measuring osmotic pressure, is ever worked out, it will be developed along this line. That is, differences of pressure rather than the enormous totals will be measured. It is hoped that the electrolytic method of making semipermeable membranes, when developed by

further study, may do away with what has hitherto appeared to be an insurmountable obstacle in the way of progress in this direction.

Contributions from the Chemical Laboratory of Cornell University.

ON BILIRUBIN, THE RED COLORING-MATTER OF THE BILE.

By W. R. Orndorff and J. E. Teeple.

[PRELIMINARY PAPER.]

The bilirubin used in this work was prepared from ox gall-stones, which were sent to us by Mr. F. M. Bell, of the firm of Armour & Co., of Chicago. We desire here to express to this company our appreciation of their kindness and generosity to us. The work here given would have been impossible but for their aid in furnishing the gall-stones free of all charge. We have used 0.75 pound of the gall-stones in this investigation. The dried gall-stones were ground, sieved through a 30-mesh sieve, and after being placed in filter-paper cylinders, extracted with ether in a Soxhlet apparatus until exhausted (twelve to twenty hours). The material was then dried and exhausted with chloroform in the same way (thirty to forty hours); again dried, placed in a porcelain dish, and extracted with boiling distilled water until exhausted. The red-colored mass was then digested for several hours with an excess of dilute hydrochloric acid, washed by decantation until the filtrate was free from calcium and hydrochloric acid, dried thoroughly, and extracted in a Soxhlet apparatus, first with ether (two hours) then with absolute alcohol until the alcoholic filtrate had only a yellow color (six hours). After drying, the material was placed in a Soxhlet apparatus and exhausted with pure chloroform (one hundred and twenty-five hours). Fresh chloroform was used after every eight hours. The chloroform extracts, containing the bilirubin, were concentrated by distillation, the concentrated solution precipitated with absolute alcohol, and the mixture heated on the water-bath until all the chloroform had distilled off. The alcohol was decanted off and the precipitated bilirubin was

boiled with absolute alcohol until exhausted. This bilirubin was found not to be completely soluble in chloroform. It was then dissolved in chloroform by heating to boiling with a large quantity of chloroform in successive portions, the solution filtered twice, concentrated, again precipitated by absolute alcohol, washed with alcohol, filtered, dried, and, if not completely soluble in chloroform, the process was repeated. All this work with chloroform and bilirubin was done in a photographic dark-room. Some of the product completely soluble in chloroform was then crystallized from pure dimethyl aniline (boiling-point 192°.2 to 192°.8 C.). This product, under the microscope, was beautifully crystallized in reddish-yellow needles and was homogeneous.

In order to determine whether the products were pure, the following analyses were made for us by Mr. G. W. Cavanaugh, of the Agricultural Experiment Station, to whom we wish here to express our thanks:

I. 0.269 gram bilirubin gave 17.7 cc. N/10 NH_3 or 0.02478 gram N.

II. 0.3444 gram bilirubin gave 22.7 cc. N/10 NH_3 or 0.03178 gram N.

	Calculated for $(C_{16}H_{18}N_2O_3)x$	Found. I.	II.
N	9.81	9.21	9.23

No. II. was heated with the sulphuric acid for three-quarters of an hour longer than No. I. These analyses were made by the modified Kjeldahl-Gunning method, adopted by the Association of Official Agricultural Chemists, 1898, and given in Bulletin 46 (revised), page 17, of the U. S. Department of Agriculture, Division of Chemistry. The formula generally accepted for bilirubin ($C_{16}H_{18}N_2O_3$), requires 9.81 per cent N.[1] Suspecting some loss of nitrogen by this method, we then made an analysis by the Chenel[2] modification of the Kjeldahl method and obtained the following result:

0.2158 gram bilirubin gave 14.12 cc. N/10 NH_3 = 0.01982 gram N or 9.19 per cent N.

[1] The atomic weights used in this paper are those recommended by the committee of the German Chemical Society. Ber. d. chem. Ges., 31, 2761 (1898).

[2] Bull. soc. chim. (Paris), 1892, [1], 321.

All three of these analyses were made with the bilirubin crystallized from dimethyl aniline. This product was completely soluble in chloroform and left no ash on ignition.

We next determined the nitrogen by the absolute method, using marble (which had been boiled for a long time with water to remove air) and dilute hydrochloric acid to generate the carbon dioxide. The following are the results with the same product analyzed by the Kjeldahl method:

I. 0.2208 gram bilirubin gave 19.2 cc. N at 732 mm. bar. (corrected) and 24°.5 C.

II. 0.1728 gram bilirubin gave 15.25 cc. N at 729.8 mm. bar. (corrected) and 26° C.

I.	II.
9.36	9.39

As we found it absolutely impossible to get carbon dioxide free from air from marble we made it by the action of boiled dilute sulphuric acid on a boiled solution of sodium bicarbonate. Using the product crystallized from dimethyl aniline and completely soluble in chloroform we obtained the following result:

0.1659 gram bilirubin gave 14.2 cc. N at 733.95 mm. bar. (corrected) and 25°.8 C. or 9.17 per cent N.

We next used magnesite to develop the carbon dioxide. This was heated in a hard-glass tube on a separate small combustion furnace. Following a suggestion of Professor Morse, we heated the copper oxide and the reduced copper spiral in the combustion tube in an atmosphere of carbon dioxide and allowed it to cool in the same gas in order to expel occluded air. A specimen of crystallized bilirubin, which was not completely soluble in chloroform, but left an infinitesimal residue, gave the following result:

0.1659 gram bilirubin gave 14.2 cc. N at 748.8 mm. bar. (corrected) and 27° C. or 9.3 per cent N.

Another analysis of a product precipitated from chloroform by alcohol, and completely soluble in chloroform, resulted as follows:

0.2084 gram bilirubin gave 17.45 cc. N at 742 mm. bar. (corrected) and 24° C. or 9.16 per cent N.

None of the products analyzed left any ash on ignition, and all were dried to constant weight at 130° C. before being analyzed.

Averaging the three results by the Kjeldahl method, gives 9.21 per cent N, while the average of the five results by the absolute method is 9.28 per cent N. If we omit the two results by the absolute method (9.36 and 9.39), where we used marble to develop the carbon dioxide (which we proved to contain air), the average of the three remaining results is 9.21 per cent N. These results agree very well with that recently obtained by v. Zumbusch[1] on bilirubin crystallized from dimethyl aniline and analyzed by the Kjeldahl method. He obtained 9.3 per cent N. Recalculating this from v. Zumbusch's data, using the same atomic weights we have specified above, would give 9.26 per cent N.

Having thus shown that our product was pure and that the formula for bilirubin, $(C_{16}H_{18}N_2O_3)_x$, is not correct, we next determined the amount of carbon and hydrogen in bilirubin, using the method given in Gattermann's Praxis des organischen Chemikers (third edition), for analyzing organic compounds containing nitrogen. Using the product precipitated from chloroform by alcohol, perfectly soluble in chloroform, and dried at 130°, we obtained the following result:

0.205 gram bilirubin gave 0.5048 gram CO_2 and 0.1133 gram H_2O = 67.15 per cent C and 6.19 per cent H.

With the product crystallized from dimethyl aniline, which was not completely soluble in chloroform, but left a minute residue (the same product which gave 9.3 per cent N (see above)), we found:

0.2336 gram bilirubin gave 0.5761 gram CO_2 and 0.1248 gram H_2O or 67.25 per cent C and 5.99 per cent H.

As it seemed possible from the results of Benedict[2] that the reduced copper spiral might have retained enough carbon dioxide or other carbon compound to vitiate the results, and, as it was also probable that any oxides of nitrogen which were not decomposed by the reduced copper spiral would also give

[1] Ztschr. physiol. Chem., 31, 454.

[2] This JOURNAL, 23, 343.

high results for carbon, we next made two analyses by the Benedict[1] method of determining carbon and hydrogen in nitrogenous organic compounds. The following are the results on the product precipitated from chloroform by alcohol, completely soluble in chloroform and dried to constant weight at 140° C.:

	Weight bilirubin.	Weight sugar.	CO_2 found.	CO_2 from sugar calculated.	CO_2 from bilirubin.	H_2O found.	H_2O from sugar calculated.	H_2O from bilirubin.
I.	0.2594	0.1270	0.830	0.19595	0.63405	0.2078	0.07355	0.13425
II.	0.3025	0.1348	0.9504	0.2080	0.7424	0.23995	0.07805	0.1619

In percentages these results are for No. I: C = 66.66, H = 5.80; for No. II: C = 66.93, H = 6.00.

At our request Dr. F. G. Benedict, of Wesleyan University, Middletown, Conn., made two analyses of this same bilirubin for us by his own method. We desire here to thank Dr. Benedict for his kindness in this matter. The following are the results he obtained:

	Weight bilirubin.	Weight sugar.	CO_2 found.	CO_2 from sugar calculated.	CO_2 from bilirubin.	H_2O found.	H_2O from sugar calculated.	H_2O from bilirubin.
I.	0.1504	0.1126	0.5411	0.1737	0.3674	0.1543	0.0652	0.0891
II.	0.1512	0.1017	0.5253	0.1569	0.3684	0.1409	0.0589	0.0820

Or, in percentages, C = 66.62, H = 6.64 for No. I; and C = 66.45, H = 6.08 for No. II. A check analysis of the sugar resulted as follows:

0.2026 gram sugar gave 0.3123 gram CO_2 and 0.1181 gram H_2O.

	Calculated for $C_{12}H_{22}O_{11}$.	Found.
C	42.07	42.04
H	6.49	6.50

Averaging these four results gives 66.66 per cent C. and 6.13 per cent H. If we omit the result H = 6.64 per cent (which is manifestly too high), we obtain 5.96 per cent H as the average of the three determinations. Since 1864, when Städeler first obtained bilirubin pure, twelve analyses have been published. The average of these is C = 66.87 per cent and H = 6.36 per cent. The following table gives the percentages required by the various formulas and the averages found by us:

[1] This Journal, **23**, 343.

	I. $C_{16}H_{18}N_2O_3$.	II. $C_{32}H_{37}N_3O_4$.	III. $C_{34}H_{36}N_4O_7$.	IV. $C_{34}H_{37}N_4O_7$.	Found. Average.
C	67.07	66.755	66.61	66.50	66.66
H	6.35	6.07	5.94	6.09	5.96
N	9.81	9.37	9.17	9.155	9.21
O	16.77	17.80	18.28	18.255	18.17

Formula III agrees better with the average of the results found than any of the others. We have endeavored to determine the molecular weight of bilirubin, but so far without success.

We next heated the pure crystallized bilirubin, completely soluble in chloroform and dried at 130° C. with *pure* concentrated hydriodic acid according to the Zeisel method[1] for determining alkoxy groups. No silver iodide was formed, and hence bilirubin does not contain an alkoxy group, nor does it contain crystal alcohol.

When heated with hydriodic acid and ammonium iodide according to the method of Herzig and Meyer[2] for determining alkyl groups joined to nitrogen we obtained the following results:

I. 0.3125 gram bilirubin gave 0.120 gram AgI. Formula III. requires 0.1198 gram for one alkyl group.

II. 0.2845 gram bilirubin gave 0.1018 gram AgI. Formula III. requires 0.1091 gram for one alkyl group.

III. 0.2912 gram bilirubin gave 0.0966 gram AgI. Formula III. requires 0.1116 gram for one alkyl group.

I. and II. were made with the bilirubin crystallized from dimethyl aniline. It was completely soluble in chloroform and dried to constant weight at 120° C. III. was made with bilirubin precipitated from chloroform with alcohol. It was completely soluble in chloroform and dried to constant weight at 130° C. These results agree better with formulas III. and IV. than with any of the others.

When heated with zinc dust in an atmosphere of hydrogen, bilirubin gives products having the odor of an old pipe. Among these products the haemopyrrol of Nencki seems to be present. That bilirubin is a derivative of pyrrol there

[1] Monatsh. Chem., 6, 989.
[2] *Ibid.*, 13, 613.

seems to be no doubt from the ease with which it unites with diazo compounds even in strong acid solution.

Further work on bilirubin, especially with a view to determining its formula and constitution as well as its relations to hemoglobin, hematin, and hematoporphyrin will be undertaken in this laboratory.

CORNELL UNIVERSITY,
ITHACA, N. Y., June, 1901.

REVIEWS.

AN INTRODUCTION TO MODERN SCIENTIFIC CHEMISTRY, IN THE FORM OF POPULAR LECTURES SUITED FOR UNIVERSITY EXTENSION STUDENTS AND GENERAL READERS. By DR. LASSAR-COHN. Translated from the second German edition by M. M. PATTISON MUIR, M.A. New York: D. Van Nostrand Co. 1901. 348 pp. Price, $2.00.

As the first German edition of this book was reviewed in this JOURNAL, Vol. 23, page 88, the excellent English translation may be treated briefly.

In this unpretentious little volume, by omitting everything of lesser prominence and skilfully avoiding reefs and quicksands in chemical theory, the author has succeeded in giving a remarkably clear elementary sketch of inorganic, and of a little of organic, chemistry. The reader of to-day should be warned, however, that some may consider the title misleading, some, indeed, may consider the terms "old-fashioned" or "obsolete" more fitting than "modern," inasmuch as nowhere in the book is mention made of *the Ion*.

To those who can find profit in non-ionic chemistry, Prof. Lassar-Cohn's book is cordially recommended as one of the best, perhaps the best of its kind. E. R.

LE FLUOR ET SES COMPOSÉS. Par HENRI MOISSAN. Paris: Steinheil. 1900.

The student who consults this book, expecting to find a dry monograph, will continue to read it with the feeling that he is enjoying a delightful account of a voyage of discovery. The author has been over all the ground himself, often as the pioneer, and he tells about it in that clear, concise, and easy manner which distinguishes him even among French scientists.

The book is divided into seven chapters and a bibliography. The first chapter treats of the isolation of fluorine. The experiments of Davy, Aimé, the Knox Brothers, Louyet, Fremy, and Gore are discussed and the reasons for their failure pointed out. The author's unsuccessful experiments are frankly

stated, and we learn that the isolation of fluorine was not a lucky accident but the result of years of work. Some of the compounds with which he worked were extremely poisonous and he was compelled to stop no less than four times on account of fluoride of arsenic alone. The apparatus originally used is described in the first chapter, though the second is devoted to new forms of apparatus for obtaining fluorine. The platinum in the original model has been almost entirely replaced by copper, thereby greatly diminishing the cost. A current of 50 volts and 15 amperes gives a liter of the gas in twelve minutes, so that the preparation of fluorine has become an easy lecture-table experiment. The next chapters are upon the physical properties of the element, its action upon metals and non-metals and their compounds and a study of the products. Its action on organic substances and its organic compounds are next studied, and the final chapter deals with some of the constants and recently discovered properties of the element. The bibliography is double, chronological and alphabetical, and contains more than 570 titles. It is impossible in a review to mention even a small fraction of the important and interesting experiments described in the book. We learn that the color of fluorine is greenish-yellow, lighter and more yellowish than that of chlorine. It boils at —187° and is still active at that temperature. At —210°, though without action on water or mercury, it combines violently with hydrogen or turpentine. Many metallic fluorides resemble the oxides, but the relationship between non-metallic fluorides and chlorides is so intimate that the element clearly belongs in the chlorine family. As fluorine, deprived of hydrofluoric acid by cooling, does not attack glass, pure fluorine is easily handled in ordinary apparatus. The discovery of this fact opens a new field of investigation, in which work has begun. Little is said of the compounds of fluorine and sulphur, their study apparently coming after the completion of the book. On the whole, it may be said that the book is one that should be read carefully by every student of chemistry, for it is a model of clearness, as the work it describes is a triumph of vigorous experimentation.

FELIX LENGFELD.

DIE WISSENSCHAFTLICHEN GRUNDLAGEN DER ANALYTISCHEN CHEMIE. Von W. OSTWALD. Dritte vermehrte Auflage. Leipzig: W. Engelmann. 1901. 220 pp.

The value of this book and its important bearing on the theoretical side of analytical chemistry have already been noted in the reviews of previous editions. This enlarged edition was called forth by the recent rapid advance in the meth-

ods of elementary instruction advocated by the author, methods which he says have been adopted in a number of the larger institutions and whose general use he thinks will only be a matter of time. He has added an appendix containing a number of experiments suitable for lecture demonstrations on the principles of analytical chemistry as taught in the book. The author, by this means, hopes also to arouse others to activity in this interesting and productive field.

J. E. G.

EXPERIMENTS FOR STUDENTS IN GENERAL CHEMISTRY. By EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania, and HARRY F. KELLER, Professor of Chemistry, Central High School of Philadelphia. Fourth edition, enlarged. Philadelphia: P. Blakiston's Son & Co. 1900. 80 pp. Price, 60 cents.

This book is intended as a laboratory guide to be used with a reference book, and is a collection of experiments from various sources. The experiments are well chosen and arranged in logical order of complexity with a number of problems upon the weight and volume relations of reactions. The student is taught to observe carefully the different stages of the reactions, and must consult reference books in connection with the experiments. The book can be recommended for use in colleges and high schools when a general course in inorganic chemistry is offered, and in case a full course is not possible a selection of typical experiments could readily be made by the teacher.

J. E. G.

QUALITATIVE CHEMICAL ANALYSIS, ORGANIC AND INORGANIC. By F. M. PERKIN, PH.D., Head of the Chemistry Department, Borough Polytechnic Institute, London. London: Longmans, Green & Co. 1900. 260 pp.

The author remarks in his preface that, recognizing the difference between book students and laboratory students, he has endeavored to write a book in which theory and practice are more or less dovetailed. He has, however, only introduced sufficient theory to make it practical and at the same time clear and interesting. In the main, the inorganic part is similar to that of other works of this kind except that he has introduced the reactions in most cases and some of the recent ideas of the nature of solutions in order to explain the reactions of analytical chemistry. The author does not make this the important feature, but gives only an outline sketch of the general principles to enable the student to grasp the nature of ions and their action in solutions. He also gives in many cases several methods for the separation of the members of the different groups. In the organic part he gives some of the reactions

and methods of separation of the different groups and calls attention to the impossibility of giving a general method for the separation of organic compounds on account of their great number and the variation in their properties caused by the presence of different groups. This book might be regarded as intermediate between the very brief courses in analysis and the very complete ones which serve as reference books rather than as practical guides to analyses. It is well printed and generally attractive. J. E. G.

QUALITATIVE CHEMICAL ANALYSIS. A guide in qualitative work with data for analytical operations and laboratory methods in inorganic chemistry. By ALBERT B. PRESCOTT and OTIS C. JOHNSON, Professors in the University of Michigan. Fifth revised and enlarged edition, entirely rewritten. New York: D. Van Nostrand Co. 1901. pp. 420. $3.50 net.

In the preface the authors state that "the text has been rewritten and the order of statement in good part recast. The subject-matter is enlarged by fully one-half, though but 100 pages have been added to the book." "It has been our aim to bring the varied resources of analysis within reach, placing in order before the worker the leading characteristics of elements, upon the relations of which every scheme of separation depends. This is desired for the working chemist and no less for the working student. However limited may be the range of his work, we would not contract his view to a single routine. It is while in the course of qualitative analysis especially that the student is forming his personal acquaintance with the facts of chemical change, and it is not well that his outlook should be cut off by narrow routine at this time."

They have, at the request of teachers, introduced in a revised form the portion upon operations of analysis, which contains some of the foundations of qualitative chemistry, and which was omitted in the last edition. They have also devoted four pages to an outline sketch of the principles of solutions and ionization, and several pages to a general discussion of the periodic system.

Part II. contains the chemistry of the metals, Part III., that of the non-metals, and Part IV., directions for systematic examinations and methods of special treatments, tables, equations, problems in synthesis and the preparation of reagents.

In the portion devoted to the chemistry of the metals, the metals and their compounds are treated in a very thorough manner, the occurrence given, and all the possible reactions discussed and the composition of the compounds formed given, with the equations, in many cases, representing the reaction.

One of the very valuable features is the introduction of the references to the original authorities in the journals. Not only methods of detection, but also methods of estimating the substance by gravimetric and volumetric methods are given. In the directions for separating the groups and members of groups, very complete notes are given, covering the possible difficulties which may arise. The amount of space, 238 large pages, of which at least half consists of small type, devoted to the metals and their compounds, will convey some idea of the amount of material contained in this book, especially when we consider the very condensed form of the statements. About 120 pages are devoted to the non-metals, especially the acids, when the properties, occurrence, formation, preparation, solubility, reactions, detection, and estimation are discussed.

This book contains material which can perhaps be found in no single text-book, and which, in a condensed form, contains much of the material found in the dictionaries of chemistry. It is a very valuable reference book, both for students of advanced inorganic chemistry and teachers, and a copy should be in every chemical library and accessible to every student. The authors are to be congratulated upon the success of the book, as evidenced by the number of editions, the clear and systematic method of presentation and the collection of reactions, which it is often impossible for a student to find explained in a satisfactory and simple manner. J. E. G.